Thermodynamics

ver. 0.02

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This is a set of lectures of thermodynamics for beginning graduate students. Each 'lecture' (chapter) is constructed from relatively short 'units'[1] that focus on single concepts or propositions. These units reference each other as hypertext. These lecture notes explain thermodynamics at the graduate level based on the elementary knowledges of physics and chemistry of macroscopic phenomena.

However, this current version contains many comments that criticize or correct conventional approaches and existing textbooks, which are not required for a textbook.

Also, the part dedicated to chemical thermodynamics is still in a preliminary form, although the needed principles are all given.

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[1] just as *Perspectives on Statistical Thermodynamics* (Cambridge University Press, 2017).

1 Introduction

1.1 What is thermodynamics?

We drive automobiles that consume fuel or use batteries, and we use fridges and air conditioners to control temperatures by transferring heat, while consuming electricity. These activities are based on interconversions of various forms of energy: electrical, chemical, thermal and so on.

Thermodynamics originated as a scientific field with the goal of comprehending phenomena concerning temperature and heat within the realm of our everyday experiences. Its purpose was to understand macroscopic phenomena and explore the interconversion of different forms of energy in physics and chemistry.

There were two key observations that established thermodynamics: the first was the recognition by Mayer and Joule (→**A.9**, **7.14**) that 'heat' is a form of energy, and the second was the recognition by Carnot (→**A.8**, **8.13** or **15.2**) and by Clausius (→**8.1**) that, as a form of (transferring) energy, 'heat' is peculiar, and we must handle thermal phenomena with special care.

1.2 What are thermal phenomena?

We mentioned 'thermal phenomena,' but it may not be clear what 'thermal' or 'heat-related' implies.

To clarify, we can provide some representative examples. We intuitively understand what 'warm' or 'cold' means; we know heating water can make it boil, and rubbing wood together can produce fire. Phenomena related to these typical examples are thermal phenomena.

We may roughly say: 'Macroscopic physical phenomena in which the fundamental laws of macroscopic electromagnetism and mechanics do not hold' are thermal phenomena. For example, when there is friction, the fundamental laws of mechanics cease to hold; relative motions subside eventually, violating the law of inertia. In particular, the conservation of mechanical energy does not hold in such cases.

1.3 What foundation should thermodynamics be based on?

What is the clear meaning of the word we use daily such as 'temperature' or 'heat? According to a dictionary, "'temperature' is the degree or intensity of heat present in a substance or object." Then, 'heat' is explained as "the quality of being hot; high temperature." To avoid circularity, we must try to understand 'thermal phenomena' in terms of something we know clearly.

Since the aim of thermodynamics is to describe 'macroscopic thermal phenomena,' it must be founded on critically scrutinized empirical facts and on the logic that is accepted as legitimate in the established macro physics and chemistry.

As has been stated in **1.1** we wish to have a clear understanding of thermal phenomena at our scale (→**1.4**). Therefore, the empirical facts thermodynamics should be founded on must be empirical facts at our scale. As an empirical science, thermodynamics also tries to be free from any particular metaphysics,[2] such as mechanical Weltanschauung.[3]

Thermodynamics employs the logic and mathematics traditionally employed in macrophysics, because the backbone of macrophysics such as mechanics and electromagnetism was established before thermodynamics was completed. Consequently, for the understanding of nonthermal physics we entirely rely on this physics.

Accordingly, those who wish to understand thermodynamics ought to know elementary mechanics and electromagnetism.[4] As logic/mathematical tools, the reader should know rudimentary linear algebra and (multivariable) calculus. Rudimentary chemistry (or common sense chemistry) is also needed, although a very terse summary will be stated later (→**4.3**).

1.4 What is 'our scale'?

'Macroscopic' usually means 'observable directly by our senses.'

The macroscopic space scale ranges roughly over our size times $10^{\pm 6} \approx 2^{\pm 20}$ (1 μm $\sim$ 1,000 km), the macroscopic time scale ranges roughly over 0.1 s, the reciprocal of the frequency of our lowest audible sound, and our life scale ($\sim 10^9$ s or, roughly, $10^{\pm 5}$ days). Thermodynamics aims to precisely describe and systematize thermal

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[2] The word 'metaphysics' may mean various different things, but here metaphysics is understood as an attempt to understand the world rationally based on *a priori* principles: "our world must be such and such."

More succinctly, "Metaphysics is to expand one's cognition without synthetic judgement" [See, K. Karatani, *Transcritique: on Kant and Marx* (MIT Press 2005)]. Here, 'synthetic judgment' is judgment referring to empirical facts.

[3] The picture of the world assuming that it can be totally understood if we understand the behaviors of particles governed by mechanics. A typical example can be seen in **A.17**.

[4] Relativity and quantum mechanics, although not usually mentioned, are not excluded so far as non-thermal macrophysics is concerned.

phenomena observable in this macroscopic space-time.

1.5 Why must we seriously take our existence as human beings?

As seen in **1.4**, this exposition emphasizes 'our scale.' Why are we, human beings, in the foreground? Isn't science objective and independent of human beings?

It is often said that the so-called empirical science is a logical summary of the world observed objectively, detached from the human beings.[5] Still, we cannot experience the world apart from our being human beings. Whatever our experiences are, they are events we human beings take part in through our bodily sense organs (and nervous systems), so it is obvious that we cannot directly recognize phenomena occurring away from our scale (→**1.4**). Therefore, empirical sciences inevitably respect our scale; the foundation of science is: Je pense et sens, donc Je suis.[6]

Against this 'primitive' assertion, there may be an objection that we have various devices such as microscopes, telescopes, etc.

We cannot say that what we see through a telescope is an image of an object that really exists in the world simply by looking at the world through the telescope. We trust telescopes, because many people can confirm the correspondence between the actual object and its telescopic image. Then, we extrapolate this correspondence to the objects we cannot directly confirm. One might add that the explanation of the principle by geometrical optics also reinforces our trust in the telescope. Needless to say, to this end we trust our logic and mathematics. Besides, what is demonstrated

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[5] According to T. Tanaka *Development of Physical World Picture* (Iwanami, 1988) Max Planck emphasized in his *Die Einheit des physikalischen Weltbildes* (*The unity of Physical World Picture*) [However, I failed to find any directly quotable statements in the original article corresponding to the following summary.]: "Science starts with empirical observations that depend on human beings, but, once established, they turn into objective reality apart from the presence of human beings. That is, the progress of science is a step-by-step approach toward objective understanding that does not depend on the human framework."

This sounds very reasonable, but facts supporting science must be verified empirically. Empirical verification is impossible apart from the human being. This fact remains even after the verification. Thus, the characterization of the progress of science according to Planck (summarized by Tanaka) is meaningless. Besides, we should not forget that this conclusion depends on the logic we regard legitimate.

Incidentally, the statement "once established, they turn into objective reality" even suggests that the fact not established by human beings does not exist objectively, a statement reminiscent of some postmodern philosophy (See, for example, A. Sokal and J. Bricmont, *Fashionable Nonsense—Postmodern intellectuals' abuse of science* (Picador USA, New York 1998).

[6] unifying Descartes (1596-1650) and Gassendi (1592-1655).

by geometrical optics is that there is a direct correspondence between the actual object and the image we observe. That is, however sophisticated the observation is, its basis is our direct sensory recognition. Therefore, to construct the physics for the understanding of the phenomena at our scale is the very foundation of the totality of physics as an empirical science.

Empirical science is an intellectual activity based on the *immediacy of experience principle* that we must be skeptical about what we cannot directly experience.[7,8]

1.6 Two categories of our experiences

Empirical sciences are based on our experiences through our bodily senses (and nervous systems[9]), but these experiences are not simply the totality of our experiences

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[7] The last chapter of D. L. Everett, *Don't Sleep, There Are Snakes, Life and language in the Amazonian jungle* (Pantheon 2008) eloquently describes the immediacy of experience principle.

"Hey Dan, what does Jesus look like? Is he dark like us or light like you?"

I said, "Well, I have never actually seen him. He lived a long time ago. But I do have his words."

"Well, Dan, how do you have his words if you have never heard him or seen him?"

They then made it clear that if I had not actually seen this guy (and not in any metaphorical sense, but literally), they weren't interested in any stories I had to tell about him. Period. (p266)

Then from p270 and on:

I began to seriously question the nature of faith, the act of believing in something unseen. Religious books like the Bible and the Koran glorified this kind of faith in the nonobjective and counterintuitive—life after death, virgin birth, angels, miracles, and so on. The Pirahãs' values of immediacy of experience and demand for evidence made all this seem deeply dubious.

However, interestingly, there might be a historical fact related to Jesus. It is certain that Mary was pregnant before her marriage to Joseph; "Usually, when such potentially damaging stories appear in the Gospels, it indicates that the underlying oral or written tradition was simply too persistent or well-known for the writer to ignore." (Jean-Pierre Isbout, *Search for the Historical Jesus* (The Teaching Company, 2022)). Additionally, the name of the true father of Jesus, a Roman soldier named Tiberius Julius Abdes Pantera (22 BCE-40 CE), was mentioned in Celsus' work, *The True Discourse* (ca. 178 CE). Very interestingly, in 1859, his tomb was discovered in Germany, revealing that this soldier was indeed stationed in Palestine until 9 CE (Jean-Pierre Isbout, ibid.). However, most historians do not consider Celsus' account to be credible.

[8] However, we must not forget that "to believe only what one sees," and "to think with one's own brain" are also hotbeds of "anti-scientism," "conspiracy theories," etc. See C. D. Ruiz and T. Nilsson, "Disinformation and echo chambers: How disinformation circulates on social media through identity-driven controversies," J. Public Policy & Marketing **42**, 18 (2022). These may be bundled as the so-called "naive empiricism." Its crucial characteristic or defect is to ignore or to make little of phylogenetic experiences (→**1.6**)

[9] For example, the law of inertia may be incorporated in the neurons connecting the retina and the visual cortex. See Johnson et al., Position representations of moving objects align with real-time position in the early visual response eLife **12**, e82424 (2023).

since birth. For example, the mechanism from the photoreceptor cells to our brains supporting vision is constructed in such a way that all our sensory inputs as to our surrounding world are consistent. We are not born in the state of *tabula rasa*, but in the state resulting from the evolution process of the past three gigayears (3 Ga); we were born in the state in which the totality of our ancestors' experiences since life was born is built in, so to speak. For example, the three-dimensionality of the world at our scale is built in (or hard-wired) in the semicircular canals. There are two categories of experiences, experiences during our lifetime and those during our phylogeny.

Even if we collect all the empirical facts, science is not possible. Especially in physics we wish to find the logic unifying the collection of empirical facts. This is the task in which our central nervous system is directly involved. It is a very interesting question in what sort of worlds organisms with logical capability can evolve. The author does not have the answer to this question, but the fact that the shapes of fishes reflect fluid dynamic properties of water strongly suggests that our having logical capability is a reflection of the logical and lawful nature of the world we have evolved in. Needless to say, our nervous system is not *tabula rasa* when ontogenetically formed.[10]

It is not always the case that our direct experiences are consistent with our logic we regard natural. In such cases, mathematical logic takes priority, because phylogenetically accumulated empirical facts must be the most reliable empirical facts.[11]

1.7 What is the characteristic of thermodynamics?

Thermodynamics is a mathematically consistent system to try to understand macroscopic thermal phenomena on the basis of the facts that are as immediately (→**1.5**) empirical as possible.

Thermodynamics is a physics diametrically different from the physics with rooms for mythological fictions that aims at answering the questions such as "what is the world made of?" or "How did the world begin?".[12] The most important cultural value of thermodynamics may reside here.

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[10] See K. Lorenz, *Behind The Mirror: A Search for a Natural History of Human Knowledge* (Harcourt Brace Jovanovich, 1977).

[11] Even the so-called tautology is a property of our world that is sufficiently stable. Perhaps there is nothing trivial that is analytic (in Kant's sense) in the world.

[12] See, for example, S. Hossenfelder, *Existential Physics*—a scientist's guide to life's biggest questions (Viking, 2022).

1.8 Non-thermal macrophysics is the basis

The basic strategy to construct thermodynamics is to extend the already completed basic laws of non-thermal macrophysics to understand empirical facts of macroscopic thermal phenomena. Here, non-thermal macrophysics whose basic laws are complete is represented by mechanics and electromagnetism,[13] but relativity and quantum mechanics are not excluded as long as macrophysics is concerned.

Only nonthermal macrophysics is available to supply bases and scaffolds for us to construct thermodynamics (except for chemistry); observables and concepts about thermal phenomena are not understood as objects of physics before constructing thermodynamics. We are allowed to use only concepts and observables that have nothing to do with 'heat', when we try to describe thermal phenomena and to construct thermodynamics. In other words, we must build thermodynamics, assuming we know only macrophysics unrelated to thermal phenomena.

Consequently, apparatuses preventing any involvement of 'heat,' and changes that do not produce any 'heat' (that is, changes for which nonthermal macrophysics holds) turn out to be the crucial conceptual and experimental devices. The former is the 'adiabatic wall' (→**7.7**) and the latter is the 'reversible quasistatic process' (→**6.6**)

1.9 Two restrictions imposed on thermodynamics

Even if thermodynamics is completed, we will not be able to realize a general and ambitious theoretical framework that allows us to understand all the thermal phenomena of any macroscopic systems. There are two fundamental restrictions.

(1) Not all the states of a given system can be understood. Only the states can be discussed in which no change can be observed by us macro-observers (called 'equilibrium states').[14]

(2) Equilibrium states of not all the macroscopic systems can be understood. Only the systems can be discussed such that, when divided into halves,[15] each half must have exactly the half energy of the original system (the system must be 'additive'

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[13] Here, 'basic laws' imply the elementary basic parts such as Newton's laws of mechanics. 'Complete' does not mean that we have understood everything macroscopically mechanical or electromagnetic. We still have tons of things our understanding of which are incomplete such as nonintegrable mechanical systems or electromagnetism of complicated materials.

[14] There is no theoretical framework that allows us to understand all 'nonequilibrium states.' There is a framework called 'nonequilibrium thermodynamics' that can discuss states slightly deviated from 'equilibrium states,' but it is not a big deal.

[15] We assume the original system is macroscopically spatially uniform.

→**2.13**).[16]

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[16] assuming the same energy origin is adopted for all the energy measurements.

A Appendix: From the theory of heat to thermodynamics

This Appendix provides an overview of the prehistory of thermodynamics.[17] The actual exposition of thermodynamics will begin in Section 2. By reading through this appendix, readers will realize how meager empirical facts originally supported the so-called chemical thermodynamics. This historical contingency still appears to impede the exposition of thermodynamics today.

A.1 Before 'modern' heat theory

Although temperature has been of interest since ancient times due to its relevance to medicine, interests in devices that could convert 'heat' into work did not gain much attention. Despite the fascination with firearms, this did not lead to the concept of a relationship between the 'ordinary' slow motions and 'heat'.

Particles or the element of fire were conceived, so 'heat' and chemistry (or its precursor, alchemy) were inseparable. Chemistry aimed to comprehend the diversity of the material world, but its strategy vacillated between the two extremes, monism and pluralism. Monism assumed that the fundamental substance was unique, but the diversity of its motions and interactions produced the materialistic diversity of the world. In contrast, pluralism assumed that there were various particles to begin with. The success of the Newtonian mechanics encouraged the monistic approaches to understand the diversity of materials in terms of the diversity of forces that interacted among particles.[18]

However, the limitation in the monistic approach that attributes all material complexity to force complexity was gradually recognized, and chemistry was systematized by Boerhaave's[19] *Elementa Chemiae* (1732) in terms of pluralistic materials theory and the element of fire: ⟨fire⟩. Contemporaneously, it was recognized from the publication of Newton's then unpublished manuscriptsx that he had conceived 'ether' long before. This with the increasing interests in electromagnetic phenomena made ⟨fire⟩ acceptable as related to Newton's ether. It was also during 1730-40 when

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[17] The author heavily relies on an excellent book: Y. Yamamoto, *Historical development of thermodynamic thoughts* 1-3 (Chikuma 2008-2009) to construct the narrative outline, although the units on Carnot **A.6** and **A.7** considerably deviate from this book.

[18] **⟪From the preface to *Principia*⟫** Newton wrote in author's preface to *Principia* (the following English translation is taken from the first US version published by D. Adee in 1846), "I wish we could derive the rest of the phenomena of nature by the same kind of reasoning from mechanical principles; for I am induced by many reasons to suspect that they may all depend upon certain forces by which the particles of bodies, by some causes hitherto unknown, are either mutually impelled towards each other, and cohere in regular figures, or are repelled and recede from each other; which forces being unknown, philosophers have hitherto attempted the search of nature in vain; but I hope the principles here laid down will afford some light either to this or some truer method of philosophy."(*Principia*, author's preface (May 8, 1686).)

[19] Herman Boerhaave (1668-1738) `https://en.wikipedia.org/wiki/Herman_Boerhaave`

Linnaeus' *Systema naturae*[20] was published, and when reductionism was critically reassessed (e.g., the reevaluation of the empiricism of Bacon).[21]

A.2 Beginning of the modern heat theory

The modernization of chemistry and heat theory was initiated by Black[22] of Glasgow.

His teacher Cullen[23] criticized Boerhaave for ascribing most qualities to corresponding particular elements and adopted repulsive forces due to thermal ether and affinities (selective attractive forces meaning intrinsic tendency for various substances to bind in multifaceted fashion) as the conceptual framework to unify understanding of chemical phenomena. As a result, affinity and repulsive force become the central issues of chemistry.

Black adopted the fact that two objects in contact reaching states without any further change indicate the same temperatures as the foundational universal law of heat theory. As can be seen from this, the invention of thermometers was the key to the development of modern heat theory.[24]

Black demonstrated that he could introduce the concept of heat capacity operationally which was consistent with the idea that 'heat' was conserved: when two objects at different temperatures are brought to equilibrium through thermal contact, the ratio of the temperature changes of these two objects is the inverse ratio of their heat capacities.[25] Black viewed the heat capacity as the strength of a certain chemical attractive force between 'heat substance' and the ordinary substance. That is, his heat theory was along the extension of Cullen's chemistry, which attempted to systematize chemical reactions in terms of selective attractive forces and repulsive forces, and was a source of the later 'caloric theory' of Cleghorn[26] and Lavoisier.[27]

The heat theory starting from Black was a source of thermodynamics, but no heat engines appeared. There was one more source, also in which caloric was deeply ingrained.

A.3 Steam engines before Watt

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[20] *Systema naturae, sive regna tria naturae systematice proposita per classes, ordines, genera, & species* (Leiden: Haak 1735). `https://en.wikipedia.org/wiki/Systema_Naturae`

[21] Francis Bacon (1561-1626) `https://en.wikipedia.org/wiki/Francis_Bacon`

[22] Joseph Black (1728-1799) `https://en.wikipedia.org/wiki/Joseph_Black`.

[23] William Cullen (1710 -1790) `https://en.wikipedia.org/wiki/William_Cullen`

[24] The modern thermometer was invented by Galileo, but the mercury thermometer was invented by Fahrenheit (1686-1736) `https://www.youtube.com/watch?v=vPmZohDmgwo`. For Celsius' contribution, see `https://www.youtube.com/watch?v=rjht4oAByCI`.

⟪**Remark on temperature**⟫ Here, what we can observe directly are the temperature changes and whether thermal equilibrium is achieved or not. We cannot directly observe 'heat.' Therefore, 'temperature' is the fundamental quantity for heat theory. However, notice that this is a historic view when heat theory was not a part of physics but an independent discipline (or perhaps a part of chemistry). In thermodynamics, heat theory must be a part of macrophysics. Concepts and quantities directly concerning 'heat' are not operationally fundamental, and must be derived as a subordinate concept from the concepts and quantities more fundamental in physics.

[25] Let C_1 and C_2 be the heat capacities of the individual objects. From $C_1\Delta T_1 + C_2\Delta T_2 = 0$, we get $C_1/C_2 = |\Delta T_2/\Delta T_1|$.

[26] William Cleghorn (1751-1783) `https://www.uh.edu/engines/epi1956.htm`

[27] Antoine Lavoisier (1743-1794) `https://en.wikipedia.org/wiki/Antoine_Lavoisier`

The idea to produce work through converting heat did not appear to exist till the modern era since Hero's 'aeolipile'[28]. For the modern idea of heat engines the discovery of vacuums was crucial.[29] As the Magdeburg hemispheres *Magdeburg hemisphere*demonstrated, the power of atmospheric pressure was overwhelming. Papin[30] invented a device that utilizes atmospheric pressure to push a piston into a cylinder in which a vacuum was created by cooling the vapor in it (1690).

At about the same time Savery[31] obtained a patent for a practical lifting pump.[32] There was a strong incentive in England to solve the flooding problem of coal mines. Newcomen[33] who was born in Devon, the birthplace of Savery, perfected an atmospheric engine by 1710, based on a similar principle as Papin's atmospheric engine.[34]

A.4 Watt and his engines

Watt[35] was an instrument maker with his shop in University of Glasgow, who had good personal relationships with distinguished professors such as Black (→**A.2**). He came from an intellectual family, and his assets were his intelligence and good personality.[36]

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[28] Hero of Alexandria (ca. 10-70 CE) https://en.wikipedia.org/wiki/Hero_of_Alexandria.

[29] ⟪**Significance of the discovery of vacuums**⟫ As stressed by Yamamoto the greatest discoveries in modern physics regarding gases were the discoveries of atmospheric pressure and vacuum by Torricelli (1608-1647), Pascal (1623-1662), and von Guericke (1602-1686). This was a groundbreaking revelation that distinguished the medieval from the modern era, and its significance is second only to the heliocentric theory. Even Galileo explained the inability of water to be lifted more than 10 meters by the competition between the aversion of air to vacuum and the force of gravity.

The dramatic demonstration of atmospheric pressure is best exemplified by von Guericke's public experiment in Regensburg in 1654, known as the Magdeburg hemispheres. An actual reenactment of the experiment, where horses are used to pull apart the hemispheres, can be seen in the following video: https://www.youtube.com/watch?v=IIQC8iEnCIY.

[30] Denis Papin (1647-1713), https://en.wikipedia.org/wiki/Denis_Papin.

[31] Thomas Savery (ca. 1650-1715) https://en.wikipedia.org/wiki/Thomas_Savery.

[32] For an explanation of the principle of his pump, see https://www.youtube.com/watch?v=0vK80s2WEno. As can be seen from this video, vapor pushes water up, so the work is not solely due to atmospheric pressure. How an actual device installed at a mine works is illustrated in https://www.youtube.com/watch?v=Dt5VvrEIj8w (after around 1min 10 sec). In principle, the pump could lift water from any depth. However, the contemporary precision of metal work caused leaks and high pressure boilers were prone to explosion, so in practice the work was done by atmospheric pressure.

[33] Thomas Newcomen (1664-1729), https://en.wikipedia.org/wiki/Thomas_Newcomen.

[34] Newcomen and his engine (with Watt's engine as well) are depicted in https://www.youtube.com/watch?v=QltRwiu4U2Q. To understand the mechanism alone https://www.youtube.com/watch?v=9GqVQPMCtY4 is recommended. An actually restored engine can be seen in https://www.youtube.com/watch?v=4DZxwGoNI5Q; https://www.youtube.com/watch?v=HC6LUWSBXjk is more faithful to the original.

[35] Jame Watt (1736-1819), https://en.wikipedia.org/wiki/James_Watt.

[36] His personal relationships with his friends and business partners were always congenial and long-lasting [https://en.wikipedia.org/wiki/James_Watt].

In the winter of 1763-4, he was asked to repair a model of Newcomen's engine (Fig. A.1 Left). The model consumed a lot of fuel. When steam is introduced to the cylinder, it must be hot, but to make a vacuum, it must be cool. In short, the same cylinder must be alternately hot and cool, wasting a lot of heat. He realized that the cylinder could be maintained hot, if the steam could be cooled in a separate cooler (condenser; Fig. A.1 Right).

The epoch-making development after the separate condenser was the 'expansion principle,' which Watt patented in 1782. Watt observed that the steam, after pushing the piston, gushed into the condenser, wasting its ability to do work. Thus, he stopped supplying steam before the piston moves all the way to the end of the cylinder and let the steam cool while expanding and doing work (the expansion principle). This resulted in 2.5 times more work produced from the same amount of fuel. Later, Carnot held Watt's expansion principle in high regard, saying that Watt was the first to use steam under gradually decreasing pressure.

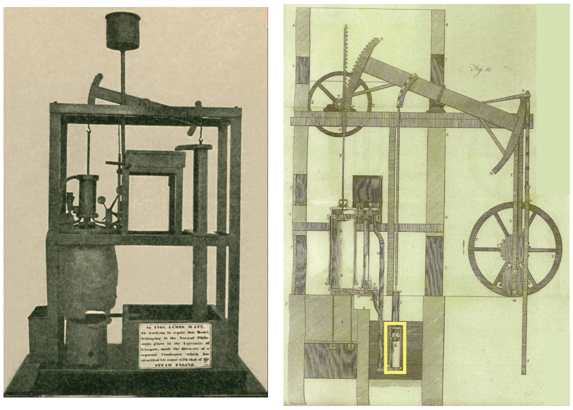

Figure A.1: The very model of Newcomen's engine Watt repaired; Right: An atmospheric engine improved by Watt. [Fig. of `https://en.wikipedia.org/wiki/Watt_steam_engine`]

Fig. A.1 The actual Newcomen engine model Watt repaired.
The plate says: 'In 1764, James Watt. In working to repair this Model, belonging to the Natural Philosophy Class in the University of Glasgow, made the discovery of a separate Condenser, which has identified his name to with that of the STEAM ENGINE.'.
Right: An atmospheric engine improved by Watt. The yellow box shows the separate condenser.

Thanks to this principle, it was discovered that the higher the steam temperatures, the more powerful the engines became. Woolf made high pressure engines practical (1814), which was not only powerful, but also fuel-efficient.

A.5 Applications of steam engines outstripped science[37]

Remarkable historical facts before the development of thermodynamics were the extensive applica-

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[37] We must not forget that the economical foundation of the Industrial Revolution was colonialism and slavery [see Eric Williams, *Capitalism and Slavery* (The University of North Carolina,1944; 3rd Edition 2021)]. HP of University of Glasgow had the following statement (which is removed now):

tions of steam engines to transportation.

Trevithick's[38] steam locomotive 'Puffing Devil' was made in 1804, and the opening of Stephenson's[39] Stockton-Darlington railway was 1825.[40] On the opening day of the Manchester-Liverpool railway, September 15th, 1830, eleven-year-old Joule (→**A.9**) went to see the trains to the suburbs of Manchester with his elder brother; there was obviously no thermodynamics whatsoever.[41]

Applications to ships were even older, as smaller engines were not necessary. In 1807, Fulton[42] connected New York and Albany (240 km) in 32 hours with a ship powered by Watt's engine.

Turner's painting of 1839: "The fighting Temeraire tugged to her last berth to be broken up, 1838" symbolizes the era.[43]

Watt's great scientific and engineering achievements are rightly celebrated. But it is also true that his family profited through the trade in slave-produced goods (such as sugar, rum and cotton from Antigua and other Caribbean islands) and on occasion they were actively involved in the purchase and sale of enslaved people. In March 1762, for example, Watt's brother John arranged for the shipment of a young boy, who was quite likely enslaved, from the Caribbean to Glasgow.

In later years, Watt undoubtedly made money by producing machinery for businesses in the Caribbean which owned enslaved people. On the other hand, during the Haitian revolution in 1791, Watt is on record cancelling an order placed by a French farm for a steam engine intended for the colony of Saint Domingo (now Haiti). Watt writes: "We sincerely condole with the unhappy sufferers, though we heartily pray that the system of slavery so disgraceful to humanity were abolished by prudent though progressive measures."

We cannot celebrate the achievements of James Watt and other great men and women of the Enlightenment without remembering their society's complicity in race slavery and imperialism, and without acknowledging that our present-day experience and understanding of race developed out of the attempts of Enlightenment thinkers to address the basic contradiction between professing liberty and upholding slavery.

[38] Ricard Trevithick (1771-1833), https://en.wikipedia.org/wiki/Richard_Trevithick.

[39] George Stephenson (1781-1848), https://en.wikipedia.org/wiki/George_Stephenson.

[40] Stephenson's locomotive model made of glass is seen in https://www.youtube.com/watch?v=73txXT21aZU. A replica of his 'Rocket' is given in https://www.youtube.com/watch?v=yNn0LC_9imY; why it lacked brakes is explained in https://www.youtube.com/watch?v=3woUopc1ZS4. The history up to Rocket can be seen in https://www.youtube.com/watch?v=w0GYZC-IJPQ.

[41] Also noteworthy is that Clapeyron supervised the construction of the first railway line between Paris and Saint-Germain; In 1835, upon authorization of a line from Paris to St. Germain, Clapeyron and Lamé (who left shortly thereafter to accept the chair of physics at the École Polytechnique) were charged with direction of the work. [based on Milton Kerker, "Sadi Carnot and the Steam Engine Engineers," Isis **51**, 257 (1960) footnote 15]. According to Kerker, "(Clapeyron was) specializing in the design and construction of steam locomotives. In 1836, he traveled to England to order some locomotives that would negotiate a particularly long continuous grade along the Saint-Germain line. When the illustrious Robert Stephenson declined to undertake the commission because of its difficulty, the machines were built in the shops of Sharp and Roberts, according to the designs of Clapeyron. He extended his activities to include the design of metallic bridges, making notable contributions in this area."

[42] Robert Fulton (1765-1815), https://en.wikipedia.org/wiki/Robert_Fulton; Robert Fulton's biography: https://www.youtube.com/watch?v=2w6x5QdswYE.

[43] The painting is explained in https://www.youtube.com/watch?v=8O-fna8HrWw&list=WL&

A.6 Father and son Carnot

In England steam engines were greatly improved during the Napoleonic Wars, so the information did not spread to France. After the wars ended in 1815, France was shocked by the progress in England, particularly by the practical high pressure engines (→**A.4**). In France, not so abundant in coal resources, saving fuel was emphasized and Woolf engines (→**A.4**) were built already in 1815. However, it was not understood why high pressure engines had good fuel efficiency. The answer was given by Carnot later on. His work was heavily influenced by his father Lazare Carnot,[44] and the caloric theory (→**A.2**) played a crucial role.

On the Continent, taking advantage of its non-flat terrain, utilization of water power was highly developed. L. Carnot was one of the engineers who completed the study of maximizing the efficiency of water powered machines.

L. Carnot generalized the principle of the loss of 'energy' due to inelastic collisions to the machine actions in general.[45] In his *On machines in general* (1782)[46] he mentioned two conditions to obtain the maximum efficiency of hydraulic machines: (1) losing all the fluid movement by its action on the machine, and (2) by insensible degrees without any percussion. (1) means all the energy is transferred to the machine, and (2) implies that the transfer must be quasistatic. A universality statement can also be found, claiming that if (1) and (2) are satisfied, independent of the actual mechanism of the hydraulic machines maximum efficiency can be realized. When Carnot wrote that there was a complete theory for machines that do not obtain motion from heat, he must have had his father's theory in his mind.

Carnot[47] visited his father in 1821, who had exiled himself to Magdeburg. It is almost certain that they discussed the problems of steam engines, since L. Carnot had been interested in the engine built in Magdeburg in 1818. After returning to Paris, Carnot wrote up his later famous paper in 1822-3.

A.7 Basic consideration by Carnot

`index=3`. C. Scallen, *Museum Masterpieces: The National Gallery, London* (Great Courses) "Lecture 22 British and French Masters c. 1785-1860" contains a nice introduction to this masterpiece.

By the way the impressionist style of paintings by Turner, Monet, and others depict trends in 19th century air pollution partly due to rampant use of steam engines. See A. L. Albright and P. Huybers, Paintings by Turner and Monet depict trends in 19th century air pollution, Proc. Nat. Acad. Sci. **120**, e2219118120 (2023). There is a followup exchange for this article: M. F. Marmor, Most paintings by Turner and Monet show stylistic evolution, not changes in pollution, Proc. Nat. Acad. Sci. **120**, e2302177120 (2023) and a reply to it by the authors: Reply to Marmor: Multiple perspectives for appreciating the meaning and beauty of Turner and Monet paintings Proc. Nat. Acad. Sci. **120**, e2303372120 (2023).

[44] Lazare Nicolas Marguerite, Count Carnot (1753-1823) https://en.wikipedia.org/wiki/Lazare_Carnot.

[45] See, for example, the Borda-Carnot equation https://en.wikipedia.org/wiki/BordaCarnot_equation.

[46] Its English translation is published in Phil. Mag. in several parts: https://babel.hathitrust.org/cgi/pt?id=mdp.39015035394322&view=plaintext&seq=314 (LIX).

[47] Nicolas Léonard Sadi Carnot (1796-1832),
https://en.wikipedia.org/wiki/Nicolas_Lonard_Sadi_Carnot.

Carnot observed: According to established principles at the present time, we can compare the motive power of heat to that of a waterfall with sufficient accuracy. Then, using the caloric theory, he considered the heat engine under the following two premises:

(1) Wherever there exists a temperature[48] difference, we can produce power.[49]

The work is produced by a steam engine not because caloric is consumed, but because caloric moves from a hot body to a cold body.

(2) A practical condition for a working substance to produce power is that it can overcome certain resistances in their changes of volume. [This is Watt's expansion principle.]

Notice that (1) is the analogy between the flow of water with a height difference and the flow of caloric with a temperature difference, and (2) is the analogy between the water pushing the blade and the expanding working substance pushing the piston.

Carnot then translated L. Carnot's quasistatic condition for the maximum efficiency machine (→**A.6**) as follows: the maximum efficiency is realized through operating the machine quasistatically; the exchange of heat must be between the systems at the same temperatures and the pressure difference must be infinitesimal.[50] The ideal engine that realizes the maximum efficiency must be reversible in the sense that the process can be reversed by supplying exactly the same amount of work that the engine produced. Carnot must have thought that all the transfer was gentle and infinitesimal, so the process could be reversed only with higher order differences.

A.8 Carnot's theorem

Carnot considered the maximum efficiency engine working between a high temperature heat source (furnace) at temperature T_H and a low temperature heat source (condenser) at temperature T_L as a cycle, following the basic consideration of L. Carnot (as explained in **A.7**). According to the argument in **A.7** a higher efficiency engine is not conceivable, but the efficiency could still depend on a particular working substance. Carnot demonstrated, using the reversibility of a maximum efficiency engine, that the maximum efficiency is universal as illustrated in Fig. A.2.[51] That is, the maximum efficiency is not dependent on the working-substance.

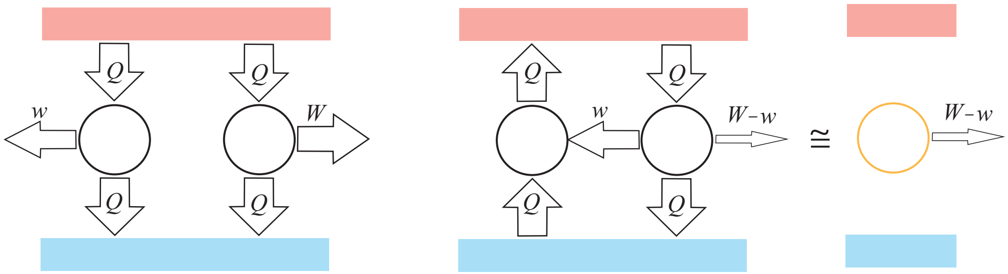

Figure A.2: It is impossible to exceed the efficiency of the Carnot engine.

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[48] Needless to say, here 'temperature' is an empirical temperature in the heat theory since Black.

[49] "Wherever there exists a difference of temperature, wherever it has been possible for the equilibrium of the caloric to be re-established, it is possible to have also the production of impelling power."

[50] Use of infinitesimal without any question reflects the wide acceptance of analysis in France.

[51] Notice that, if we use the modern terminology, the proof demonstrates: "Carnot's theorem must be true because energy is conserved." (a wrong reason)

Fig. A.2 Left: The left engine is the Carnot engine = the maximum efficiency engine, and the right engine is a supposedly more efficient engine that can produce more work $W > w$ from the same heat Q.
Center: Since the left engine is reversible, using a part of the work supplied by the 'better' engine, it can be operated as a caloric pump. Consequently,
Right: The whole device is equivalent to a perpetuum mobile producing work $W - w > 0$ without any supply of caloric (i.e., adiabatically).

A.9 Mayer and Joule: conservation of energy

Mayer,[52] on a voyage to Java as a ship's doctor, became interested in thermal phenomena and came up with the idea that all the phenomena in the world depend on the changes in materials and their interactions caused by ⟨force⟩ and that the total amount of ⟨force⟩ is conserved, with only its quality changing." From the requirement of conservation of ⟨force⟩ and the fact that 'motion' disappears by the two-body inelastic collision, he concluded that heat and work were both forms of ⟨force⟩, and that they could mutually interconvert under a fixed law (1841). Then, he provided the conversion rate of heat and work for the first time, considering the Mayer cycle (→**14.8**).

Independently from this, Joule[53] demonstrated that the constancy of the heat-work conversion rate (the so-called *work equivalent of heat*) using various phenomena.

Thus, it was established that thermal energy is a form of energy, and that the sum of mechanical energy and thermal energy is conserved, if correctly converted, for all the physical phenomena.

However, this observation was not immediately widely accepted. Conceptually, the biggest obstacle was Carnot's theorem (→**A.8**), which was understood to imply the nonequivalence of heat and work. For example, Thomson recognized the significance of Joule's work, but was troubled by the apparent contradiction with Carnot's theorem, and believed further empirical facts were needed.

A.10 How did Clausius proceed?

Clausius's[54] thinking was as follows.[55] As Mayer and Joule had demonstrated (→**A.9**), if consumption of work produces heat, heat is not conserved. Therefore, it is natural and logical to assume that when work is produced, heat is consumed. Therefore, other than the 'first principle' that the sum of heat and work is conserved, he postulated the following principle:[56]

> In all cases work results from heat, an amount of heat proportional to the work produced is consumed, and, conversely, the same amount of heat can be produced by consuming an equal amount of work.

It is important to note that the work-heat equivalence holds only when work results from heat.

As noted in **A.7** in Carnot's original idea caloric = heat was conserved. However, this idea

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[52] Julius Robert von Mayer (1814-1878), `https://en.wikipedia.org/wiki/Julius_von_Mayer`.

[53] James Prescott Joule (1818-1889), `https://en.wikipedia.org/wiki/James_Prescott_Joule`.

[54] R. Clausius (1822-1888) `https://en.wikipedia.org/wiki/Rudolf_Clausius`.

[55] R. Clausius, Über die bewegende Kraft der Wärme und die Gesetze sich daraus für die Wärmelehre selbst ableiten lassen, Annalen der Physik **155** 368 (1850).

[56] `https://archive.org/details/ueberdiebewegen00claugoog/page/n11/mode/2up` p7

contradicts the above principle. Therefore, the engine converts only a part of heat into work. Clausius found that if there were a more efficient engine than the reversible engine, Carnot's logic (→Fig. A.2 in **A.8**) in the proof of his theorem implies that heat flows from a lower temperature[57] heat source to a higher temperature heat source without any other trace. Since such a process can never occur naturally, Clausius concluded that work is done only if heat flows from a higher to a lower temperature heat source and that if heat cannot flow from a lower temperature heat source to a higher temperature heat source without any other trace, then Carnot's theorem can be proved (Fig. A.3).

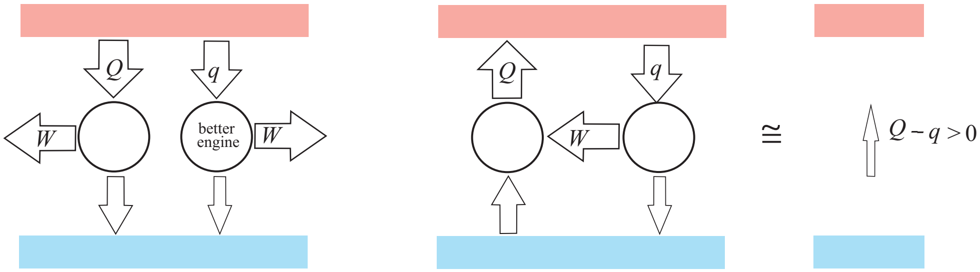

Figure A.3: If heat can flow from a lower to higher temperature heat source, then Carnot's theorem does not hold.

Fig. A.3 Left: The left empty circle denotes a reversible engine, which may be used as a heat pump if work W is supplied. The 'better engine' on the right is a hypothetical engine with a better efficiency, which requires heat q ($< Q$) from the higher heat source to produce the same amount of work W.
Center: If the better engine drives the reversible engine backward as a heat pump, heat $Q - q > 0$ is given to the higher heat source.
Right: According to the 'first principle,' this heat must have come from the lower temperature heat source. Therefore, 'heat flows from a lower temperature heat source to a higher temperature heat source without any other trace.' This is against the general experience that temperature differences naturally diminish and cannot spontaneously increase.

Thus, Clausius' paper of 1850 established the foundation of thermodynamics.[58]

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[57] Here, 'temperature' is an empirical temperature in the tradition of heat theory.

[58] E. A. Guggenheim, *Thermodynamics* (Fifth, revised edition, North Holland 1967) p17 says: The second law was foreshadowed by the work of Carnot (1824). The first and the second laws were co-ordinated by Clausius (1850) and by Kelvin (1851).” quoting Clausius Ann Phys Lpz 1850 79 368, 500 and Thomson Trans Roy Soc Edinb 1853 20 261. Notice that Thomson acknowledged Clausius' priority in his early manuscripts (albeit not straightforward) [(according to Yamamoto ibid., p086 of III) quoting p324 of C. Smith and M. N. Wise, *Energy & Empire, a biographical study of Lord Kelvin* (Cambridge UP, 1989): “... in an early draft of his 1851 published paper 'On the dynamical theory of heat':

> The same conclusion has been arrived at by Clausius, to whom the merit of having first enunciated and demonstrated it is due. It is with no wish to claim priority that the author of the present paper states that *more than a year ago* he had gone through all the fundamental investigations depending on it which are at present laid before the Royal Society, at that time

A.11 Interpretation of the second law in terms of 'equivalent'

In a 1854 paper, Clausius interpreted the second law as claiming that any non-spontaneous transformation cannot occur without compensation by a spontaneous transformation.

> The transformation of producing work from heat that cannot occur spontaneously cannot occur without compensation by a spontaneous transformation that transfers heat from a higher temperature object to a lower temperature object.

In other words, there are two kinds of transformation of energy, spontaneously possible and not. Non-spontaneous transformations never occur without being compensated by spontaneous transformations. Reversible transformations are the changes in which both kinds of transformations balance.

Consider the following two spontaneous processes:
A: Process converting work W into heat at temperature θ;
B: Process converting heat Q at temperature θ into heat Q at temperature θ' $(< \theta)$.
Their reversed processes are denoted as A^{-1} and B^{-1}, respectively.

In a process that actually happens, A^{-1} is compensated by B (an engine), and B^{-1} is compensated by A (heat pump). Transformations that can be substituted for each other are regarded as equivalent transformations. To express this equivalence quantitatively, Clausius introduced a quantity called the 'equivalent of transformation' which is proportional to the relevant energy and additive with respect to the connection of successive transformations so that the total equivalents of a reversible process is zero. The equivalent of a spontaneous transformation is chosen to be positive as follows:

The equivalent of A is $Wf(\theta)$,

The equivalent of B is $QF(\theta,\theta')$ with the sign convention $F(\theta,\theta') > 0$ for $\theta > \theta'$.

The equivalents of the reversed transformations are: $-Wf(\theta)$ for A^{-1}, and $QF(\theta',\theta)$ for B^{-1}. The additivity implies $QF(\theta,\theta') + QF(\theta',\theta)) = 0$, so we require

$$F(\theta,\theta') = -F(\theta',\theta). \tag{A.1}$$

A.12 Carnot engine in terms of Clausius' equivalents

Carnot's reversible engine may be interpreted as follows (Fig. A.4):
Engine direction: Heat $Q_H - Q_L$ at temperature θ_H is transformed into work W and the process is compensated by the natural transformation converting heat Q_L at temperature θ_H into heat Q_L at temperature θ_L.

> considering the conclusion as highly probable even should Carnot's hypothesis be replaced by the contrary axiom of the dynamical theory; and that more recently succeeded in convincing himself demonstrative of its truth, without any knowledge of its having been either enunciated or demonstrated previously, except by Carnot.[footnote 16: William Thomson, Early draft of the 'Dynamical theory of heat', PA132, p. 10. Our emphasis. ...]

On p327 of the same book, we find: "In whatever way one judges Thomson's independence from Clausius, his interaction with Rankine during 1850 was crucial." On p325 we read "Rankine's response to Clausius's first paper on the motive power of heat (published earlier that year in Poggendorff's *Annalen*) reinforced Thomson's awareness of the need for new 'proof' of Carnot's criterion...."

Heat pump direction: Work W is naturally converted to heat $Q_H - Q_L$ at temperature θ_L, while compensating the transformation of heat Q_H at temperature θ_L into that at temperature θ_H.

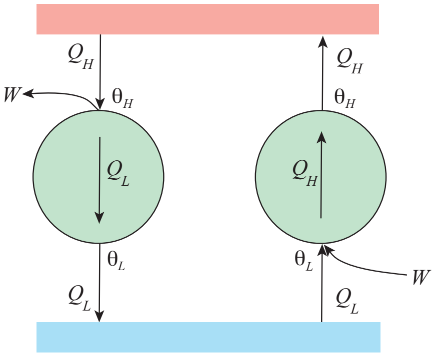

Figure A.4: Carnot's reversible engine interpreted in terms of equivalent compensation; Left: heat engine, Right: heat pump.

For reversible processes the total equivalent must be zero: for the reversible engine

$$-Wf(\theta_H) + Q_L F(\theta_H, \theta_L) = 0, \tag{A.2}$$

and for the reversible pump

$$Wf(\theta_L) + Q_H F(\theta_L, \theta_H) = 0. \tag{A.3}$$

Adding the above two formulas with the aid of (A.1), we get

$$W[f(\theta_L) - f(\theta_H)] + [Q_L - Q_H]F(\theta_H, \theta_L) = 0. \tag{A.4}$$

The 'first principle' implies $W = Q_H - Q_L$, so the above formula implies

$$f(\theta_L) - f(\theta_H) = F(\theta_H, \theta_L) > 0. \tag{A.5}$$

Hence, $f(\theta)$ is a monotone decreasing function. Therefore, Clausius introduced a monotone increasing function $T(\theta)$ [59] as

$$T(\theta) = 1/f(\theta). \tag{A.6}$$

Thus, we have the following summary:

(1) The equivalent of the process of converting work W $(= Q)$ into heat Q at temperature T is Q/T.

(2) The equivalent of the process of heat Q transferred from heat source at temperature T_H to that at T_L is $Q/T_L - Q/T_H$.

(1) agrees with the equivalent of heat Q from temperature $T_H = \infty$ to $T_L = T$ in (2). Thus, Clausius concluded that work is equivalent to an infinite temperature heat.

Furthermore, (2) may be interpreted algebraically as the sum of the equivalent of absorbing heat Q at temperature T written as Q/T; the high temperature heat source absorbs heat $-Q$ whose

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[59] This is still an empirical temperature, but actually identical to the absolute temperature (→**11.6**).

equivalent is $-Q/T_H$.

Here T is not the temperature of the system but the heat source. Furthermore, the sign convention of Q is 'seen from the heat source.' Thus, the process of heat source releasing $|Q|$ is with $Q < 0$. [Remark: This sign convention is the opposite of the usual thermodynamic convention (→**7.1**) which is system-centered.]

A.13 Clausius was almost reaching entropy

Suppose there are many heat sources with temperature T_i. For a process in which heat Q_i is absorbed by the ith heat source, the equivalent of the process is

$$N = \sum \frac{Q_i}{T_i}. \tag{A.7}$$

If there are numerous heat sources and if we may use differential expressions, then

$$N = \oint \frac{dQ}{T}. \tag{A.8}$$

Consider a cycle, where the system exchanges heat with the sources and returns to the original state. Suppose $N < 0$ for this cycle. This means that the cycle cannot occur spontaneously. If $N > 0$ and if the cycle is reversible, then $N < 0$, so for a reversible cycle only $N = 0$ is allowed.

(A.8) implies that the integral of dQ/T is conserved in reversible processes. Apart from the sign convention, N is just 'entropy' (→**14.5**). However, it took Clausius ten years to introduce 'entropy', eventually in 1864.

A.14 Clausius' twists and turns

As we have seen up to **A.13** Clausius almost reached the concept of 'entropy,' which is a thermodynamic quantity of central importance, through the idea of equivalent and compensation (→**A.11**). However, there were processes for which 'equivalents' could not be computed, because the principle of the equivalents of transformations could not be used. For example, take an adiabatic free expansion (→**17.12**). The gas does not do any work nor exchange any heat, but the process is irreversible, so there must be a remaining positive 'equivalent.' How much is it? This cannot be obtained by considering transformations as 'heat $\Longleftrightarrow$ external work' and 'high temperature heat $\Longleftrightarrow$ low temperature heat' alone.

Clausius solved this problem as follows: He divided internal energy into real heat corresponding to the translational kinetic energy and the rest. Then, he thought the work to the latter as 'internal work,' and conceived the two transformations, 'heat $\Longleftrightarrow$ real heat' and 'heat $\Longleftrightarrow$ internal work.' Then, he wrote $dQ = dH + dQ'$, where dH is the real heat and dQ' is the rest. From this he wrote

$$\frac{dQ}{T} = \frac{dH}{T} + dZ. \tag{A.9}$$

He interpreted the volume increase as internal work, and 'equivalent' Z was assigned to it. He named Z ⟨disgregation⟩ (1862). The naming suggests that Clausius thought of it as measuring the extent of irreversibility due to the spread/diffusion of material. Clausius thought dZ depended only on volume V.[60] Then, dZ is exact. Therefore, Clausius concluded (in the 'modern' saying) that as the sum of two exact differentials $dS = dQ/T$ is exact; S is named 'entropy.' Thus, entropy change is due to diffusions of heat and of matter.

Although Clausius removed any mention of ⟨disgregation⟩ from his 1876 reprint of his entropy papers, his twists and turns were not useless. 'Thermal chemistry' was grafted to ⟨disgregation⟩ (→**A.15**).

A.15 Horstmann and the beginning of chemical thermodynamics[61]

Horstmann,[62] who attended Clausius' thermodynamics lectures at ETH in 1866, applied the ideal gas law to the ⟨disgregation⟩ part of entropy as $dZ = (P/T)dV$ and calculated the $dZ = (P/T)dV$ of substance A as

$$Z_{\mathrm{A}} = Z^0_{\mathrm{A}} - R\log(P_{\mathrm{A}}/P_0). \tag{A.11}$$

He considered the reaction A $\longleftrightarrow$ B. When the extent of reaction is ξ for the reaction (→**25.9**),

$$\Delta Z(\xi) = (Z_{\mathrm{B}} - Z_{\mathrm{A}})\xi. \tag{A.12}$$

If the reaction heat is Q (per unit reaction), the entropy change can be expressed as

$$\Delta S = \frac{Q\xi}{T} + \Delta Z(\xi). \tag{A.13}$$

Applying the entropy maximization principle as the equilibrium condition

$$Q/T + \frac{dZ}{d\xi} = Q/T + (Z_{\mathrm{B}} - Z_{\mathrm{A}}) = Q/T + \Delta Z^0 + R\left(\log(P_{\mathrm{A}}/P_0) - \log(P_{\mathrm{B}}/P_0)\right) = 0. \tag{A.14}$$

Thus, we have

$$\log(P_{\mathrm{A}}/P_{\mathrm{B}}) = -Q/T - \Delta Z^0. \tag{A.15}$$

That is,

$$\frac{P_{\mathrm{A}}}{P_{\mathrm{B}}} = Ce^{-Q/T}. \tag{A.16}$$

This relation was experimentally verified.

Thus, the condition for chemical equilibrium, or the criterion for equilibrium, is given in the form "If the entropy of the system is denoted as S, then at equilibrium, δS must be equal to zero". This provision is considered to be the pioneering theoretical content and this Horstmann's work

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[60] If we use the modern thermodynamics

$$dZ = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV. \tag{A.10}$$

[61] T. Inoue, "Formation process of dissociation equilibrium by A. Horstmann—Beginning of chemical thermodynamics in the latter half of the 19th century." Kagakushi Kenkyu II **26**, 1 (1987).

[62] August Friedrich Horstmann (1842-1929) https://en.wikipedia.org/wiki/August_Friedrich_Horstmann.

was regarded as a demonstration of the applicability of the entropy theory to chemistry.

van't Hoff[63] pursued application of thermodynamics to chemistry, influenced by Horstmann's work: "According to Horstmann, the principles of thermodynamics is applicable to chemistry."[64] However, the supporting facts were no more than what is summarized above.

A.16 Faraday, Joule and quantitative applications of electrochemistry

Faraday[65] demonstrated all the electricities (bioelectric, electricity by magnetic induction, electricity from batteries, etc.) were identical, and the quantity of electricity was measured in terms of the consumption of zinc of the Daniell cell. That is, electrochemistry was indispensable in measuring charge and current. Faraday established Faraday's law: a chemical equivalent corresponds to a definite amount of electricity. Joule constructed a galvanometer in 1839 and even proposed a standard method to quantify electricity.[66] Joule's law as to Joule heating was discovered while pursuing the relation between the amount of electricity and heat. The work equivalent of heat was for the first time measured through converting work into electrical energy.

A biographer of Joule summarized[67] his work as follows: through measuring electric action, Joule was able to trace a definitive quantity of physical effect throughout the entire field of physics.

Notice that the foundation of his work was electrochemical in nature.

A.17 What did Helmholtz say about chemical energy?[68]

At the end of his exposition, "On the conservation of force"[69] Helmholtz[70] discussed the combustion of coal.

The carbon and oxygen atoms adhere firmly to form a new compound in combustion: "this attraction between the atoms of carbon and of oxygen performs work just as much as that which the earth in the form of gravity exerts upon a raised weight." "When carbon and oxygen atoms have rushed against each other, the newly-formed particles of carbonic acid must be in the most violent molecular motion—that is, in the motion of heat."

Can we reverse the process? Plants just do that. An easier example is the electrolysis of water. To this end electric current must be supplied from a Galvani cell, but it is produced by oxidation of metal. That is, to return water, a combustion product, to hydrogen gas another 'combustion

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[63] Jacobus Henricus van 't Hoff Jr. (1852-1911) See https://en.wikipedia.org/wiki/Jacobus_Henricus_van_%27t_Hoff.

[64] M. J. H. van't Hoff, *Etudes de dynamique chimique* (1884), p124.

[65] Michael Faraday (1791-1867), https://en.wikipedia.org/wiki/Michael_Faraday.

[66] O. Reynolds, *Memoir of James Prescott Joule* (Manchester Literary and Philosophical Society, 1892) p42.

[67] O. Reynolds, ibid., p66.

[68] "Chemical energy" here means energy in general associated with chemical reactions in an informal fashion.

[69] Hermann von Helmholtz, *On the Conservation of Force* Introduction to a Series of Lectures Delivered at Carlsruhe in the Winter of 1862-1863 (Translated by Edmund Atkinson). "Force" means energy throughout his exposition just as in Mayer's writings (→**A.9**).

[70] Hermann von Helmholtz (1821-1894). https://en.wikipedia.org/wiki/Hermann_von_Helmholtz.

reaction' is used; to overcome a chemical force another chemical force[71] is used, but the current may be produced by magnetic induction as well.

Thus, Helmholtz used a mechanical toy model of chemical reaction and electrical energy-chemical energy equivalence 'to establish' the law of conservation of energy unifying, electromagnetism, mechanics, heat theory and (electro)chemistry.

A.18 How about the second law for chemistry?

Helmholtz' rhetoric 'established' the conservation of energy as the most general principle of the world. His article quoted in **A.17** was immediately translated into English. This indicates the importance of his exposition.

However, the first law is not truly a thermodynamic principle. The second law is the key. Thus, van't Hoff appreciated Horstmann's demonstration as we have seen in **A.15**. Notice that this was likely the only work on the applicability of entropy to chemical reactions before Gibbs, who introduced chemical potential in his epoch-making work.[72] Is there any statement justifying that 'chemical coordinates' (or the amounts of chemical) may be handled in the same way as usual work coordinates, as opposed to heat? No, there is none. Helmholtz's mechanical model hypnotized thermodynamics.

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[71] Notice that chemical force = chemical energy in Helmholtz writing.

[72] J. W. Gibbs, "On the equilibrium of heterogeneous substances," Trans. Connecticut Academy, III 108 (1875-6), 343 (1877-8).

2 Preliminary I: Equilibrium states

2.1 What is a macroscopic system?

Throughout these lecture notes, a 'system' implies an object of our scale (→**1.4**) occupying a definite spatial domain.[73] Its boundary is macroscopically definite. The system boundary is definite due to walls made of a certain material (as in the case of a gas in a canister) or perhaps the boundary of the system itself (as in the case of a solid block).

For macroscopic systems if their sizes increase, the amounts of physical quantities (e.g., its mass) carried by (or immediately associate with) the boundary walls become less significant relative to those carried by the system bulk, so we ignore the effects of the physical quantities carried by the walls. Therefore, the effect of a wall is only to impose a boundary condition to the system under consideration, mathematically speaking, so 'wall' and 'boundary condition' will be used interchangeably. Inserting a new wall in a system is interpreted as imposing a boundary condition between the parts created by insertion of the wall.[74]

The world surrounding a given system is called the *environment* of the system.[75]

2.2 What sort of states of macroscopic systems do we wish to understand?

Even if a system is macroscopic (→**1.4**), its state can be diverse; an explosion may have just occurred inside or is 'dead' for a long time so macro-observers like us cannot discern any change. If a system is changing in time and is not spatially homogeneous, in order to describe its state even macroscopically, a small number of observables must not be sufficient. Therefore, it is sensible to start with aiming at understanding the simplest states first, and then to use the results to construct a fuller theory to understand more general states.

If a macrosystem is left for a sufficiently long time in a constant environment (that

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[73] Its boundary is macroscopically two-dimensional (not fractal) just as an ordinary block.

[74] We can say that systems whose walls are allowed to be abstracted as boundary conditions may be studied by thermodynamics. Thus, information thermodynamics that utilizes mesoscale examples with very clear boundary conditions like boxes are often dubious.

[75] Here, the word 'world' is used, but, in practice, it is a small portion of the world that surrounds the system and has immediate interactions with the system.

does not cause 'dissipation'[76]), very often the system reaches a state in which 'nothing happens.' Such a state is called an equilibrium state. Thus, 'thermodynamics'—the theory of heat, work and energy transformations—aims, to begin with, at a theoretical system to describe 'equilibrium states' and their quasistatic changes (→**A.6**) precisely.

2.3 What is an equilibrium state?

It was stated at the end of **2.2** that a state is called an equilibrium state in which nothing happens and that is reached eventually by a macrosystem left for a sufficiently long time in a constant environment (→**2.1**). The terms used in this statement may be fairly clear, so the meaning of 'equilibrium state' may be clear. However, still the meaning of the following terms should be better specified: "constant environment," "sufficiently long time," "leaving," "eventually," and "nothing happens" (→**2.4**-**2.6**).[77]

2.4 "Nothing happens"

"Nothing happens" in our context means that no time dependence can be observed within our space-time scale (→**1.4**).[78]

If our space-time resolution is much finer than our scale, then we could observe space-time dependent phenomena called 'fluctuations'. However, they are averaged out at our scale.

In thermodynamics, "nothing happens" means that there is no time dependence for any macroscopic observables.

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[76] A system has no dissipation when the macroscopic energy conservation law holds (→**3.10**).

[77] Some supposedly mathematically rigorous expositions assume 'equilibrium state' as a primitive concept, so it is not defined. The present exposition will not adopt a pseudo mathematical approach but try to be as operational as possible (that is why, e.g., atomistic explanations are avoided).

The fundamental problem of a formal or mathematical system is that the relation between the actual world and the world of logic/mathematics is not usually specified. We are interested in natural science, so any theoretical framework must be firmly grounded on the actual phenomena in the world. Thus, very explicit description of the relation between the theoretical system and the actual phenomena must be in the theoretical system for natural science. In these lecture notes, we assume that the macrophysics and chemistry are sufficiently founded on the 'rough ground' (as said by Wittgenstein in 107 of *Philosophical Investigations* (Blackwell Publishers, 1953 50th anniversary commemorative edition)).

[78] We may roughly say that the time scale in the range of $2^{\pm 20}$ days and the length scale $2^{\pm 20}$ m.

2.5 “Sufficiently long time”

In **2.4**, the long time scale is set to be $\sim 10^6$ days, but if we wait longer, some change may happen.

If the time scale we are interested in is, for example, a day, then if nothing happens even if we wait for 10 days, we may practically say that there is no change for a sufficiently long time.

Feynman states roughly as follows: if all the fast processes that should happen have happened and if all the slow processes that might happen have not yet started significantly, then the system is in equilibrium.

“Eventually” implies, ideally, ‘forever after’, but, as implied above, actually or in practice the word implies that our observation time scale is much longer than the time scales of all the fast events in the system (and still no extremely slow processes have started).

2.6 “Constant environment”

A ‘constant environment’ implies an environment (see just below and **2.1**, esp., the last footnote) for which “nothing happens” (→**2.4**) for a “sufficiently long time” (→**2.5**). Here, we assume that the system we consider has a definite and stable boundary (→**2.1**). An environment is a part of the world that is enclosing the system and that may affect it. How the environment interacts with the system across the boundary is also specified as a property of the environment (that is, the boundary conditions between the system and its environment are the part of the properties of the environment).

Generally speaking, however, it is not so easy to specify the external environment, so often in thermodynamics, it is assumed that there is nothing outside the system; that is, it is assumed that the system is isolated from the rest of the world: The state is called an equilibrium state, if nothing happens (→**2.4**) in the system after isolating it for a sufficiently long time (→**2.5**).[79]

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[79] Precisely speaking, according to this definition of equilibrium, it is not simple, for example, to define the equilibrium state in an isothermal (= constant temperature) environment. Perhaps, we can prepare a system attached to a heat bath at a constant temperature for a sufficiently long time, and then isolate it. However, according to the definition using isolation, the system before isolation is not in equilibrium, and after isolation it is not isothermal, strictly speaking. Therefore, we need a convention or an assumption of some sort stated explicitly. For example, the state of a system is (thermodynamically) the same even if it is isolated from its original environment. Thus, we assume the partitioning-rejoining invariance **2.12** explicitly.

However, the state of a system may be constant under the effect of constant external influence. For example, the system may be under a constant electric field. Even in such cases after a sufficiently long time the system would reach a constant state, but if we take out a portion from the system and isolate it, its state should often be different from the one before isolation. Therefore, relaxing the isolation condition, we allow the imposition of static uniform fields (e.g., electric field, magnetic field, etc.) after isolating the system[80] as a condition for a “constant environment.”[81]

“Leaving” implies that we human observers/experimenters do not do anything to the system enclosed in its environment.

2.7 Definition of ‘equilibrium state’

Taking account of **2.6**, we would say:

> An equilibrium state of a system is a state without any macroscopic change after it is left for a sufficiently long time in a constant environment that does not cause any dissipation.

Needless to say, ‘constant environment’ (→**2.6**), ‘sufficiently long time’ (→**2.5**), ‘macroscopic change’ (→**2.4**) are used as specified above.

However, an equilibrium state is completely determined by its current state of the system irrespective of its history, so it may not be satisfactory to characterize ‘equilibrium’ by how it is prepared. Therefore, we prefer:

> A state of a system is an equilibrium state, if there is a constant environment in which we can embed the system with an appropriate boundary condition (wall) without causing any change of the state of the system and without any dissipation.

It is desirable to guarantee that an equilibrium state does exist, so we may add

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[80] Generally speaking, imposing a uniform external field could induce a sort of flow in the system causing ‘dissipation.’ However, if a uniform external field is imposed after the system is isolated, then usually lasting flow would not be induced, so there would be no dissipation.

‘Without dissipation’ is, roughly speaking, even if we put the system and the environment together in a Dewar jar, the temperature does not go up. Or, the system taken as a movie played backward does not look unnatural; added work to the system can be recovered completely without any trace in the system.

[81] However, as Akira Shimizu clearly points out, that there is an effect of external field from outside implies that the system allows long range interactions. Thus, we cannot say that the system is energetically additive (→**2.10**). However, still there are situations in which the system energy is additive, so we are allowed to develop an ordinary thermodynamics for such systems.

that the system left alone for a sufficiently long time in a constant environment will reach an equilibrium state. Still it should be emphasized that for the definition of an equilibrium state, how it is reached should be irrelevant.

2.8 Uniqueness of the equilibrium state

Prepare a system that is materially closed (i.e., no import/export of any matter allowed) and is left in an environment E until it reaches an equilibrium state (→**2.7**). If we repeat this experiments from the macroscopically identical initial condition in the same environment E, the final state is usually the same.[82,83]

This uniqueness is an empirical fact, so we assume this as the basic premise (principle) of thermodynamics (for simple systems →**2.9**).

2.9 Simple systems and compound systems

We wish to avoid complicated equilibrium states to begin with. In an extreme case we may prepare unrelated systems in various equilibrium states and then juxtapose them without any interaction between them to declare the resultant collection to be a single equilibrium system. Then, we may introduce various interactions (i.e., walls or boundary conditions →**2.1**) among them. Thus, we can make indefinitely complicated equilibrium systems. Still, to develop a general theory, we should start with the simplest systems.

We define 'simple systems' just below and then we assume all the systems in thermodynamics are simple systems or *compound systems* constructed from simple systems by joining them with appropriate boundary conditions as mentioned just above.

As 'simple systems,' it should be advantageous to pay special attention to the systems that are spatially homogeneous. Unfortunately, however, there is no guarantee that such a system is always spatially homogeneous irrespective of its states (perhaps phase separation could occur, for example). Therefore, we define a system to be a *simple system*, if we can actually observe the system to have a spatially uniform

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[82] Here, the adverb 'usually' appears. Precisely speaking, for simple systems (→**2.9**) the uniqueness of the final equilibrium state is always the case. Some complications could happen for compound systems (→**2.9** as illustrated in **16.7**), but such cases are very rare, so we may practically assume the reproducibility of the equilibrium state.

[83] Here, 'the same' means that we cannot discern any difference macroscopically. The precise uniqueness of the equilibrium state can only be provided after the equivalence of two equilibrium states is clearly defined. See **5.1**.

equilibrium state (under some condition).[84]

In contrast, a *compound system* is defined as a system that is not homogeneous but cannot be thermodynamically distinguished from a system made by connecting various simple systems across appropriate walls.

2.10 What sort of macrosystems do we wish to understand?

For a simple system (→**2.9**), prepare its copy.[85] Both are left in the identical spatially uniform time-independent environment E till no change is observed macroscopically. Thus, the two systems reach an identical equilibrium state (→**2.8**). Then, combine these two systems with an arbitrary boundary condition (i.e., through a certain wall →**2.1**) and leave the combined system[86] in the same environment E as a whole as illustrated in Fig. 2.1.

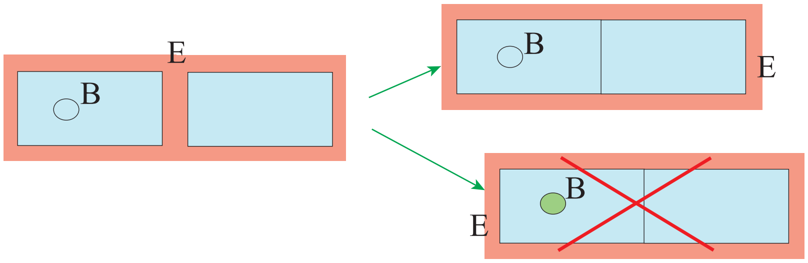

Figure 2.1: Thermodynamics deals with systems in which each small but macroscopic portion (e.g., the oval 'B') exhibits no change in its macroscopic state before and after combining with its copy. The lower right case demonstrates a disqualified scenario, where the oval (representing any macroscopic portion) undergoes a change in its state after the combination.

After a sufficiently long time, we compare the states of an arbitrarily chosen small but macroscopic volume 'B' (illustrated as small ovals in Fig. 2.1) in the system before and after the combination. We only deal with the systems that we cannot discern any macroscopic (→**1.4**) change in the above two states of 'B' for any wall between the system and the copy (Fig. 2.1). Let us call a system satisfying this invariance an *additive system*.

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[84] A simple system need not be made of a single chemical. The condition is that we can actually observe it to be spatially homogeneous under some condition.

[85] A system in a macroscopically indistinguishable state; for simplicity, let us assume the simple system is in a spatially uniform state. If you wish to be general, then the nonuniform spatial structure must be faithfully copied.

[86] such a system will be called a compound system (→**2.9**).

2.11 Nonadditivity due to long-range interactions

If the 'reaching' range of interactions between the parts of the system is not small (i.e., the decay rate of the interaction strength as a function of distance is small), the additivity (in the sense of **2.10**) may be violated. This could cause alteration of energy density as the system volume varies. Gravitational and electrostatic (Coulombic) interactions have such a property.

Gravitational interaction within the system is not significant at our scale, so in the usual thermodynamics, this is ignored.[87] Electrostatic interactions are quite large, so if there are 'naked' charges, we are not allowed to ignore them. However, if the system is electroneutral, for example, plus and minus charges could shield each other, and the electrostatic interaction range may be macroscopically infinitesimal. Thus, we may generally assume that electrostatic interactions do not cause nonadditivity.

However, if the distance between the positive and negative charges are fixed as in electric dipoles, electrostatic shielding is not complete, so the electrostatic interaction energy decays as r^{-3}, where r is the spatial distance. Consequently, the additivity mentioned above fails, and, furthermore, even if the system volume is maintained, the total energy can depend on the macroscopic shape of the system. There are many systems such as ferroelectrics containing molecules with permanent electric dipoles. The same difficulty is encountered for ferromagnetic materials for which macroscopic magnetism arises from the collection of permanent magnetic dipoles.

As we will see later, for the systems mentioned above, sufficiently general mathematical theory cannot be constructed. Thus, thermodynamics discusses only (energetically) additive systems for which the total energy[88] of the system is proportional to its volume.

2.12 Partitioning-rejoining invariance of equilibrium states[89]

If a macroscopic system is divided cleanly into two pieces of roughly equal sizes,[90] then the resultant pieces are again macroscopic systems. Here, 'dividing cleanly'

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[87] The gravitational interaction with the system and some big external bodies (e.g., the earth) cannot be ignored, but the effect is uniform over the system and appropriately handled within the thermodynamics we will develop.

[88] The origin of energy must be appropriately chosen.

[89] If uniform external fields such as an electric field are imposed, we must perform the partitioning-rejoining procedure under the same external fields.

[90] The illustration Fig. 2.2 might suggest 'brute force breaking of the system into two', but various gentle methods are possible; for example, if you wish to divide an ice block, you can melt it and then freeze it into two half blocks.

refers to a non-fractal dividing surface and the surface areas of the pieces must be proportional to 2/3 power of their volumes, if length is scaled, (such partition is called the *van Hove partition*).

If a macroscopically non-uniform system in equilibrium may be divided into small and uniform macrosystems, we have only to understand spatially uniform systems. Therefore, the following is explicitly required for convenience:[91]

> A macroscopic part of an equilibrium macrosystem is again in equilibrium.

If a macroscopic system is in equilibrium, the divided pieces are again in equilibrium.

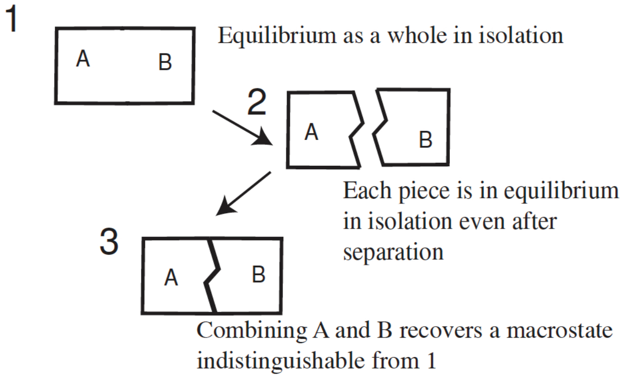

Figure 2.2: The partitioning-rejoining invariance of equilibrium states: A macrosystem is partitioned into two pieces A and B (1→2) and then rejoin them (2 → 3).

If the resultant two pieces are rejoined,[92] we get a macrosystem whose state is (thermodynamically) indistinguishable[93] from the original equilibrium state:

> An equilibrium state is partitioning-rejoining invariant. Needless to say, the constraints (walls), if any, must not be altered before and after partitioning.

2.13 Partition additivity and additivity

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[91] Actually, for the macroscopic part under consideration the rest of the system + the environment is its environment, and the part is in equilibrium with this environment, so the above requirement need not be made particularly according to the second definition in **2.7**.

[92] This rejoining may not be at the cut ends, since thermodynamic quantities/observables are shape-independent. The reader might worry about the symmetry-broken phases: must not we respect the consistency of order parameters at the connection boundary? Thermodynamics do not respect the order parameter orientations that do not affect the system internal energy, so we may ignore this consistency. The same applies to the flow that can exist in superfluid phases. We need not pay any attention to the flow field if the accompanying kinetic energy is not affected.

[93] Precisely speaking, we must clearly specify when we may say that two states are identical to tell the indistinguishability. As mentioned before, see **5.1**.

2.12 tells us that it is natural to consider physical quantities whose total amount is equal to the sum of the amounts in each part obtained by partitioning. Such a quantity is called, in thermodynamics, an *additive quantity.*

Note that here what are added are quantities carried by the parts of originally a single system, quite distinct from the ordinary additivity in mathematics.

In mathematics, a set function[94] Q is additive, if

$$Q(A \cup B) = Q(A) + Q(B) \tag{2.1}$$

for the sets A and B that are mutually exclusive: $A \cap B = \emptyset$.

In distinction, the additivity mentioned in conjunction to partitioning-rejoining invariance implies for any sets A and C

$$Q(A) = Q(A \cap C) + Q(A \setminus C). \tag{2.2}$$

That is, it is the additivity with respect to the partition of a set A into two mutually exclusive subsets. This additivity is a distinct concept from the ordinary additivity, so in these lectures, we call this additivity *partition additivity.*[95]

2.14 Thermodynamic limit

It is said in **2.12** that a macrosystem roughly divided into halves results in two macro systems, but, needless to say, we cannot indefinitely repeat this procedure to make smaller macrosystems. If we wish to do so, the initial macrosystem must be 'infinitely' large. Theoreticians are fond of thinking in this limit, so the limit has a name: the '*thermodynamic limit.*'

We have only to recognize that the systems we study macroscopically are very close to this limit.[96]

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[94] A set function is a map whose domain is an appropriate family of sets (say, a ring of sets) with its values in $\mathbb{R}$.

[95] An illustration of the need for the distinction: Consider a system with chemical reactions. In equilibrium, if we cut the system into two parts, for any chemical in the system, its total amount is the same as the sum of the amounts in the parts. That is, the total amount of any chemical does not change before and after the cut, so it is partition additive. Needless to say, the amount of a chemical is an extensive quantity (→**3.1**). If you prepare two systems with perhaps different chemical compositions and combine them to make a single system, the total amount of a chemical before and after joining can be different due to chemical reactions, so the amount of chemicals cannot be additive.

[96] 'Close' in the following sense; all the densities of extensive quantities almost agree with the limit densities (→**5.5**).

3 Preliminary II: Work coordinates

3.1 Extensive quantities

Prepare a system that is uniform at our scale (or, more precisely, a simple system →**2.9**).

As we have seen in **2.14**, in thermodynamics it is natural to consider a very large system size limit, so we should first pay attention to the quantities that increases without bound as the system size increases.

We should not, however, forget that we restrict systems we consider to a class of additive systems (→**1.9**, **2.10**): if the energy of the system depends on a quantity that is not partition additive (→**2.13**), then the partitioning-rejoining invariance of equilibrium states **2.12** would not hold. Therefore, when we consider a physical quantity Q_V that diverges as the system volume V increases indefinitely, we need not take account of the quantities for which Q_V/V is not bounded from above. If Q_V is asymptotically proportional to V and Q_V/V converges to a density which is not identical to zero, we call such quantities *extensive quantities*.

3.2 Fundamental variables are extensive variables

The quantities that increase with the system volume are not restricted to the additive quantities. For example, the surface area of the system or the accompanying surface energy is often proportional to the 2/3 power of the system mass.

Earlier it was said the theoreticians like the thermodynamic limit (→**2.14**). In this limit all the extensive/partition additive quantities diverge and become meaningless. Consequently, as the corresponding meaningful quantities, densities (extensive quantities/volume) are considered. However, then, the densities of the quantities like surface energy vanish identically in the thermodynamic limit. Accordingly, all the basic quantities describing systems in thermodynamics are extensive quantities. Volume, energy, amount of a chemical, etc., are the examples.

3.3 Thermodynamic coordinates are extensive or intensive

An extensive quantity is a first degree homogeneous function (→**3.5**) of the amounts of materials, so a fundamental variable Q of thermodynamics is a first degree homogeneous function of other fundamental (so extensive) quantities Q_i.[97] If we write $Q = Q(Q_1, Q_2, \cdots, Q_n)$, for any λ (> 0) we have[98]

$$\lambda Q = Q(\lambda Q_1, \lambda Q_2, \cdots, \lambda Q_n). \tag{3.1}$$

If Q is partial-differentiable with respect to Q_i, the corresponding partial derivative q_i is a homogeneous function of degree zero (→**3.5**(1)). That is, irrespective of λ (> 0),

$$q_i = q_i(\lambda Q_1, \lambda Q_2, \cdots, \lambda Q_n). \tag{3.2}$$

A quantity that is a homogeneous function of degree zero of the amount of materials is called an *intensive quantity*. Although not fundamental quantities (→**3.8**), intensive variables are also important and convenient in thermodynamics. As we will see later, temperature T, pressure P, etc., are the examples of intensive quantities.

3.4 Why do intensive quantities show up in thermodynamics?

As can be seen from **3.3**, the reason why intensive quantities show up in thermodynamics is not because they do not diminish as the system size increases. If that is the reason, we have to keep, e.g., all the quantities that depend on positive fractional powers of the system volume such as its surface energy. Sometimes, the general observation: "all the variables of thermodynamics are extensive or intensive" is referred to as the fourth law of thermodynamics, but its essence is captured by the fact that all the fundamental variables of thermodynamics are extensive (→**3.2**).

3.5 Homogeneous functions

Let u be a function defined on an n-cone[99] whose apex is at the origin. For any λ (> 0) if

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[97] A fundamental quantity may be regarded as a function of non-fundamental quantities as well, but such a functional form is not the basic relations in thermodynamics. For example, as we will see, the internal energy may be written as a function of temperature T. Since T is not a fundamental variable, such a functional relation is *not* a basic thermodynamic relation.

[98] Let $\{M_i\}$ denote the amounts (e.g., moles) of materials/chemicals in the system. Then an extensive quantity Q_j is a first degree homogeneous function of $\{M_i\}$. Since Q is also extensive,

$$\lambda Q(\{M_i\}) = Q(\{\lambda M_i\}).$$

Note that

$$Q(\{\lambda M_i\}) = Q(\{Q_j(\{\lambda M_j\})\}) = Q(\{\lambda Q_j(\{M_i\})),$$

so these two equalities imply that Q is a first degree homogeneous function of $\{Q_i\}$.

[99] n-cone is a subset C of n-vector space such that $x \in C \Rightarrow \alpha x \in C$ for any positive α.

there is a real number p such that

$$\lambda^p u(x_1, \cdots, x_n) = u(\lambda x_1, \cdots, \lambda x_n), \tag{3.3}$$

u is called a *homogeneous function of degree* p.
(1) If u is differentiable, partially differentiating (3.3) with x_j ($j \in \{1, \cdots, n\}$) with the aid of the chain rule, we get

$$\lambda^p \frac{\partial u}{\partial x_j} = \lambda u_{x_j}(\lambda x_1, \cdots, \lambda x_n). \tag{3.4}$$

Therefore, $\partial u/\partial x_j = u_{x_j}$ is a homogeneous function of degree $(p-1)$ for any j $(\in \{1, \cdots, n\})$.
(2) Assuming that u is differentiable, we differentiate (3.3) with respect to λ to get

$$p\lambda^{p-1} u(x_1, \cdots, x_n) = \sum_i x_i \frac{\partial u}{\partial \lambda x_i}. \tag{3.5}$$

Setting $\lambda = 1$, we find

$$pu = \sum_i x_i \frac{\partial u}{\partial x_i}. \tag{3.6}$$

(3) [**Euler's theorem for homogeneous functions**] If u is differentiable, (3.6) is a necessary and sufficient condition for u to be a homogeneous function of degree p.

To show this we have only to construct a general solution for (3.6), following the solution method of quasilinear partial differential equations (→**3.6**).

3.6 Euler's theorem for homogeneous functions

Let u be a differentiable function defined on a n-cone whose apex is at the origin.
Theorem [Euler] A necessary and sufficient condition for function u to be a homogeneous function of degree p is that the following quasilinear partial differential equation holds:

$$\sum_{i=1}^n x_i \frac{\partial u}{\partial x_i} = pu. \tag{3.7}$$

[Demonstration] If we differentiate (3.3) with respect to λ, as already noted in **3.5**(2), the chain rule gives

$$p\lambda^{p-1} u(x_1, \cdots, x_n) = \sum_{i=1}^n x_i \frac{\partial}{\partial \lambda x_i} u(\lambda x_1, \cdots, \lambda x_n). \tag{3.8}$$

If we set $\lambda = 1$, we get (3.7).

To demonstrate the converse, we have only to solve the quasilinear partial differential equation (3.7).[100] Writing its characteristic equation with a clever use of the parameter λ as

$$\frac{du}{pu} = \frac{dx_i}{x_i} = -\frac{d\lambda}{\lambda}, \tag{3.9}$$

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[100] There is an elementary explanation of the general solution method for quasilinear partial differential equations in Note 3.4 of Y. Oono, *The Nonlinear World* (Springer, 2013) p159-160.

its general solution can be written as

$$F(\lambda^p u, \lambda x_1, \cdots, \lambda x_n) = 0 \tag{3.10}$$

in terms of an arbitrary differentiable function F. That is, if u is a function of $\{x_i\}$, then $\lambda^p u$ must be a function of $\{\lambda x_i\}$, so indeed u is a homogeneous function of degree p.

3.7 Internal energy

Thermodynamics began as a branch of physics that sought to understand how the energy of a system changes due to exchange of heat and work between the system and its environment. Therefore, the energy E of the system is a necessary variable in constructing thermodynamics.

The total energy of the system includes the kinetic and potential energies as a whole. We usually observe a system from the co-moving coordinates, so the energy E relevant to thermodynamics is the total energy minus the mechanical energy as a whole (i.e., the kinetic and potential energies of the center of mass) and is referred to as the *internal energy*.[101]

It is worth reiterating that thermodynamics discusses only systems whose internal energy is partition additive/extensive (→**2.10**).

Remark In the above, the total mechanical energy is excluded from the energy in the system, but other energies associated with the system could be excluded as well, if they do not change by the processes under consideration.

3.8 Intensive variables are not fundamental variables

In rudimentary thermodynamics, temperature appears as an important variable. As we have seen in Appendix A (→**A.2**) temperature was historically crucial.[102] However, we know temperature cannot uniquely specify macroscopic states of a system

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[101] Also the system is assumed to be not rotating around its center of mass.

[102] **Empirical temperatures** For the concept of empirical temperature, two key points should be considered:
(1) Any empirical concept must be grounded upon our direct bodily senses. However, there is no reason to believe that "temperature" is a scalar quantity, as sensations of "hot" and "warm" are sensed by different mechanisms. While we tend to perceive "hot" and "warm" as only differing in extent, it is possible that our understanding of "temperature" is influenced by later-established concepts. Therefore, using empirical temperature as a foundation for thermodynamics can be logically circular.
(2) Even if one relies on metaphysical principles to believe that temperature is a scalar quantity, it is important to note that an ideal gas is just one example. To establish the universality of temperature independent of specific materials, it is necessary to demonstrate that the temperature

as illustrated by ice-water; even if the temperature is the same, the internal energy of the ice-water system can change according to the ratio of ice and liquid water present. Thus, the internal energy is a better observable to distinguish macroscopic equilibrium states.

It is easy to understand why intensive quantities are not suitable for specifying states by considering the fact that we can always devise a wall that allows two systems to share the same values of a particular intensive quantity. In contrast, we cannot devise a wall that equalizes extensive quantities of the systems in contact through it, whenever these systems equilibrate each other.

3.9 Thermodynamic coordinates, introduction

As we have already discussed, the internal energy E is a key quantity of thermodynamics, so we need it to describe the system under study.

To specify a system, we must first designate its material composition (very often, its chemical composition). To this end we can use the mole numbers $\{\tilde{N}_i\}$ of all the chemical compounds $\{i\}$ present in the system (more details later →**4.6**). Collectively, we denote the chemical composition of a given system as $\tilde{\boldsymbol{N}} = \{\tilde{N}_i\}$.

In order to describe the macrophysics of the system on this material stage specified by $\tilde{\boldsymbol{N}}$,[103] we choose a set $\{X_i\}$ of extensive observables (as actors) that are required to describe macrophysical events in the system that alter E (more details later →**3.10**). Thus, $\{X_i\}$ are called *work coordinates*, which will be collectively denoted as $\boldsymbol{X}$.

As discussed in **1.8** we may assume the quantities and concepts are unambiguous, if they are understood within nonthermal macrophysics and chemistry. Work coordinates are all understood with nonthermal macrophysics. Also we assume we have knowledge of elementary chemistry (→**4.3**).

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scale remains consistent under different materials, with a diffeomorphic relationship. Without the framework of thermodynamics, it becomes challenging to guarantee that the temperature of an ideal gas is monotonically related to the absolute temperature.

[103] However, as we will later realize (e.g., **4.5**), $\tilde{\boldsymbol{N}}$ is not a convenient way to describe the materialistic aspects of the system. This is because, unless we can freely halt chemical reactions at any given moment in the system while modifying other variables, particularly work coordinates $\boldsymbol{X}$, as assumed in standard chemical thermodynamics textbooks, this approach is highly unnatural and almost impossible to implement. Hence, when we delve into comprehensive chemical thermodynamics, we will make every effort to avoid this artificial assumption.

3.10 Work coordinates and work

If we consider only the operations without any energy dissipation,[104] to change the work coordinates $\boldsymbol{X}$ implies that the energy E is changed in a fashion we can quantify with the aid of the fundamental laws of electromagnetism and/or mechanics. There is nothing special; these are the operations on the states of the system observed in the experiments that verify electromagnetic and mechanical fundamental laws and theories. To realize such experiments often we have only to slow down the processes (quasistatic processes →**A.6**).[105] The world solely governed by the fundamental laws of macroscopic electromagnetism and mechanics is the world whose movies do not look strange even if they are played backward.[106] This is often the case, because dissipation[107] is absent. Under the condition in which dissipation can be ignored, the variation of the work coordinates is reversible in the sense that the change can be step by step retraced without leaving any trace.

When a work coordinate X_i is changed infinitesimally and reversibly, the accompanying internal energy change may be written as a *work form* $x_i dX_i$, where x_i is, as can be seen from **3.3**, an intensive quantity (something like a force) that is a function of E and $\boldsymbol{X}$ given by the nonthermal macrophysics. It is called the *conjugate intensive quantity* of X_i. Thus, generally, the work form reads

$$\omega = \sum_i x_i dX_i. \tag{3.11}$$

If the system is materially closed (→**4.3**), then the conservation law of electromagnetic and mechanical energies implies that ω is exact (→**9.10**): $\omega = dE$. This is why $\{X_i\}$ are called work coordinates.[108] Some examples of work coordinates will

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[104] ⟪**Without dissipation**⟫ 'without dissipation' implies that macroscopic electromagnetic and mechanical energies are not lost from the system (conserved). Crudely speaking, if we put the system and environment in a Dewar jar during the process, no temperature increase is detected. The dissipation may not directly be by the irreversible processes in the system itself, but also due to the production of sound or (electromagnetic) radiation. Such a production itself may be purely mechanical and/or electromagnetic, but these radiations never return to the system completely, so their production usually entail dissipation.

[105] However, quasistatic processes in electrodynamics can be pretty fast from our 'everyday' standard. The conversion rate between mechanical and electrical energies is said to be up to 95% with the conventional devices. Superconducting devices can significantly improve this number.

[106] if there is no radiation of waves (sound, electromagnetic, etc.) from the system; note, however, that if the system is enclosed in a 'isolated room' of finite size, radiation means ordinary dissipation unless there is a radiation equilibrium between the system and the room.

[107] including production of radiations as discussed in a preceding footnote.

[108] Thermodynamics does not pay any attention to the quantities that do not change energy, so

be given in Appendix B (→**B.1**-**B.3**).

Needless to say, the procedure or mechanism to alter work coordinates is realizable within nonthermal macrophysics. That is, it is assumed that electromagnetism and mechanics without any dissipation is possible, so we can construct reversible source of work macrophysically.

3.11 Changing work coordinates without thermal phenomena

As long as there is no ‘friction’[109] we may realize a change in work coordinates without dissipation. The key observation is, for example, the Joule heat loss during the transport of charges may be reduced as much as we wish by slowing down the process.

Suppose we wish to move charge q as an electric current I. If the resistance of the wire is R, the heat generation per unit time is given by RI^2 (Joule heating). The needed time is $\Delta t = q/I$, so the total amount Q of heat generated is give by

$$Q = \Delta t \times R \left(\frac{q}{\Delta t}\right)^2 = \frac{Rq^2}{\Delta t}. \tag{3.12}$$

Therefore, if Δt is large, that is, if we slow down the process, this can be made as small as we wish.

However, (3.12) tells us that slowing down by increasing R is useless.[110]

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from the potential list of work coordinates the extensive quantities are excluded whose conjugate intensive quantities are identically (macroscopically) zero.

[109] ⟪**The so-called friction**⟫ As discussed just below, if the ‘frictional force’ is proportional to the ‘changing rate’ (as viscosity in fluids), the dissipated energy is a higher order small quantity. However, for the kinetic friction due to dry friction between solids, the friction force is constant independent of the changing rate (speed), so however slow the relative motion is, the amount of dissipated energy is independent of the changing rate. Thus, quasistatic change cannot be realized however slowly we perform the process.

Precisely speaking, as Granick and his collaborators extensively studied [e.g., S. Granick, Y. Zhu and H. Lee, Slippery questions about complex fluids flowing past solids, Nature Materials **2**, 221 (2003)] what happens at the interface between a fluid phase and a solid surface is very complicated, and ‘dry friction’ (slip) can happen, although the effect is very small for ordinary fluids.

[110] Since the voltage difference is $V = Rq/\Delta t$, reducing the voltage difference V to transport the charge is the practical way to reduce dissipation.

Notice that increasing R is analogous to choking the passage, analogous to making the size of the gas leak hole smaller. Indeed, the dissipation rate decreases, but the process itself is not reversible as we will discuss later. Also slowing down chemical reactions with the aid of negative catalysts is analogous.

3.12 A slightly more general discussion

If there is no 'friction,' and if the general theory for linear transport phenomena applies, we can proceed as follows:

Suppose a small change of a work coordinate X requires energy change $dE = xdX$. Let us assume that connecting system I with $x = x^{\mathrm{I}}$ and system II with $x = x^{\mathrm{II}}$ the flow of X from I to II is driven by the difference in x. If X is conserved, then

$$\frac{d(E^{\mathrm{I}} + E^{\mathrm{II}})}{dt} = (x^{\mathrm{II}} - x^{\mathrm{I}})\frac{dX}{dt} \tag{3.13}$$

and linear transport law with transport coefficient L (like Ohm's law)

$$\frac{dX}{dt} = L(x^{\mathrm{II}} - x^{\mathrm{I}}) \tag{3.14}$$

would hold. If we streamline the above relations as

$$\frac{dE}{dt} = -\delta x\frac{dX}{dt} \tag{3.15}$$

and

$$\frac{dX}{dt} = L\delta x, \tag{3.16}$$

we have

$$\frac{dE}{dt} = -L\delta x^2 = -\frac{1}{L}\left(\frac{dX}{dt}\right)^2. \tag{3.17}$$

The minus sign is put, because we discuss the electromagnetic and mechanical energy E of the system and its decrease due to dissipation.

As can be seen from this, if we change X by ΔX in time Δt, then the total change of X is of course ΔX, but the total change of the energy due to dissipation is

$$\frac{1}{L}\left(\frac{\Delta X}{\Delta t}\right)^2 \Delta t = \frac{(\Delta X)^2}{L\Delta t}. \tag{3.18}$$

That is, even if ΔX is constant, if the needed time Δt is made sufficiently long, the total dissipation can be reduced as much as we wish.[111]

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[111] However, if the driving force is large, increasing Δt by reducing L is useless, since L and Δt appear together, as already noted at the end of **3.11**.

B Appendix B. Examples of work and work form

This topic is of the non-thermal macrophysics, so thermodynamics simply adopts the results, but, for convenience, some examples are given here.

B.1 Work due to volume change

Let us find the work form ω for a quasistatic[112] change of the system volume from V to $V + dV$. Let us write the surface area element as $d\boldsymbol{S}$ and its small displacement along the outward normal as δl (Fig. B.1).

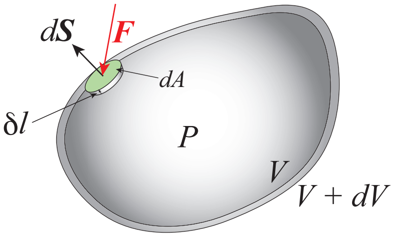

Figure B.1: Volume work

If the force per unit area $\boldsymbol{F}$ acts on the surface area element $d\boldsymbol{S}$, displacing it by δl, the work done to the system is $\boldsymbol{F} \cdot d\boldsymbol{S}\delta l$. If we collect them all over the surface of the volume, we get the volume work:

$$\omega = \int_{\partial V} \delta l \boldsymbol{F} \cdot d\boldsymbol{S}. \tag{B.1}$$

The work must be done quasistatically, so the external force per unit area $\boldsymbol{F}$ and the system pressure P at each part of the surface must be in balance. Let us denote the area of the surface element $d\boldsymbol{S}$ by dA. Then,

$$\boldsymbol{F} \cdot d\boldsymbol{S} + P dA = 0, \tag{B.2}$$

so (B.1) becomes

$$\omega = -\int_{\partial V} \delta l P dA. \tag{B.3}$$

The volume change is given by

$$\delta V = \int_{\partial V} \delta l dA, \tag{B.4}$$

and the pressure is everywhere the same during quasistatic changes, so (B.3) becomes

$$\omega = -P dV. \tag{B.5}$$

Notice that this P is the mechanical quantity and has nothing to do with thermodynamics. There is no thermodynamic pressure, but only mechanical pressure. Do not forget that all the work coordinates are defined outside thermodynamics.

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[112] sufficiently slowly; in this case slowing down also implies reversibility, because the dissipation is due to volume viscosity, so linear irreversible formalism used in **3.12** applies.

B.2 Work done by magnetic field

For the needed Maxwell's equations see **B.4**.

Magnetic field itself does not do any work directly on charged systems. The work done by magnetic field is the work done on the current by the electric field induced by the magnetic field. Thus, the term relevant to work is $\boldsymbol{J}_f \cdot \boldsymbol{E}$ due to the current $\boldsymbol{J}_f$ supplied from outside the system and $\boldsymbol{E}$. Subtracting (B.24)$\cdot\boldsymbol{H}$ from (B.24)$\cdot\boldsymbol{E}$ and ignoring the displacement current, we get

$$\boldsymbol{E}\cdot \operatorname{curl}\boldsymbol{H} - \boldsymbol{H}\cdot\operatorname{curl}\boldsymbol{E} = \boldsymbol{E}\cdot\boldsymbol{J}_f + \boldsymbol{H}\cdot\frac{\partial \boldsymbol{B}}{\partial t} \tag{B.6}$$

If we look at the formulas

$$\nabla\cdot(\boldsymbol{A}\times\boldsymbol{B}) = (\nabla_A+\nabla_B)\cdot(\boldsymbol{A}\times\boldsymbol{B}) = \boldsymbol{B}\cdot(\nabla_A\times\boldsymbol{A}) - \boldsymbol{A}\cdot(\nabla_B\times\boldsymbol{B}) = \boldsymbol{B}\cdot\operatorname{curl}\boldsymbol{A} - \boldsymbol{A}\cdot\operatorname{curl}\boldsymbol{B}, \tag{B.7}$$

the left-hand side of (B.6) reads $\operatorname{div}(\boldsymbol{H}\times\boldsymbol{E})$, so

$$\operatorname{div}(\boldsymbol{H}\times\boldsymbol{E}) = \boldsymbol{E}\cdot\boldsymbol{J}_f + \boldsymbol{H}\cdot\frac{\partial\boldsymbol{B}}{\partial t}. \tag{B.8}$$

If all the systems and relevant apparatuses are contained in a finite space, we may assume the fields decay sufficiently quickly to zero outside this space, so integrating the above formula over the whole space, we obtain

$$0 = \int dV\, \boldsymbol{E}\cdot\boldsymbol{J}_f + \int dV\, \boldsymbol{H}\cdot\frac{\partial\boldsymbol{B}}{\partial t}. \tag{B.9}$$

If we add work quasistatically, the current is constant throughout the experiment, so the strength of the magnetic field is also constant. Integrating the above equation over the whole experimental duration, and writing the total change of $\boldsymbol{B}$ as $\delta\boldsymbol{B}$, we get

$$\boldsymbol{H}\cdot\delta\boldsymbol{B} = -\int dt\, \boldsymbol{E}\cdot\boldsymbol{J}_f. \tag{B.10}$$

Since the energy is supplied by working against the current due to the change of the magnetic field, the right-hand side gives the energy supplied to the magnet with the correct sign. Therefore, the work form for the work done by the magnetic field reads

$$\omega = \boldsymbol{H}\cdot d\boldsymbol{B}. \tag{B.11}$$

If we decompose as $\boldsymbol{B} = \mu_0\boldsymbol{H} + \mu_0\boldsymbol{M}$, (B.11) becomes

$$\omega = d\left(\frac{1}{2}\mu_0\boldsymbol{H}\cdot\boldsymbol{H}\right) + \mu_0\boldsymbol{H}\cdot d\boldsymbol{M}. \tag{B.12}$$

Here, $\boldsymbol{H}$ is the magnetic field created by the device, so it exists even without the magnet. The first term is the change of the vacuum magnetic field energy. Therefore, if we remove it and regard $\mu_0\boldsymbol{H}$ as the actual external field, we get

$$\omega = \boldsymbol{B}\cdot d\boldsymbol{M}. \tag{B.13}$$

However, this is not always correct. It is correct when the so-called *demagnetizing field* can be ignored as in the case of a long magnet with the magnetic field applied parallel to its long axis. It is totally different for a spherical magnet.

This difficulty is simply due to the magnetic interaction being long-ranged (→**2.10**).

B.3 Work done by electric field[113]

Since electric field does not enter inside conductors, the electric field energy does not change according to the state of the conductor, so the state of a conductor is not altered by the external electric field.

For dielectrics, the electric field goes into the bulk of the material. Therefore, the field has a strong thermodynamic effect. Electric work is done by displacing true charges, so in terms of the true charge density change $\delta\rho$ and electric potential φ, the work may be written as

$$\delta W = \int dV \varphi \delta\rho \tag{B.14}$$

The integration here is over the volume of the dielectric. Noting that

$$\boldsymbol{E} = -\mathrm{grad}\,\varphi, \;\; \mathrm{div}\,\delta\boldsymbol{D} = \delta\rho, \tag{B.15}$$

the integration result is given by

$$\begin{aligned} \delta W &= \int_V dV \varphi\, \mathrm{div}\,\delta\boldsymbol{D} = \int dV [\mathrm{div}\,(\varphi\,\delta\boldsymbol{D}) - \mathrm{grad}\,\varphi \cdot \delta\boldsymbol{D}] && \text{(B.16)} \\ &= \int_{\partial V} d\boldsymbol{S} \cdot \varphi\,\delta\boldsymbol{D} + \int_V dV \boldsymbol{E} \cdot \delta\boldsymbol{D} && \text{(B.17)} \end{aligned}$$

We may ignore the surface contribution for macroscopic systems. Only the second term is the extensive contribution. If the electric field is uniform, the work form reads

$$\omega = \boldsymbol{E} \cdot d \int_V dV \boldsymbol{D} = d \int dV \frac{\varepsilon_0}{2} \boldsymbol{E}^2 + \boldsymbol{E} d \int_V dV \boldsymbol{P}. \tag{B.18}$$

The first term exists even for non dielectrics, so $\boldsymbol{E} \cdot d\boldsymbol{P}$ is the work density. Note, however, that this conclusion applies only for macroscopic objects.

B.4 Our convention for the electromagnetic field

In this lecture notes, we follow the ***E*-*B*** correspondence, which is the world standard, and use the SI unit system. That is, we assume all the magnetic fields are due to currents, and the Maxwell's equation in the vacuum reads

$$\begin{aligned} \mathrm{div}\,\boldsymbol{E} &= 0, & \mathrm{curl}\,\boldsymbol{E} &= -\frac{\partial \boldsymbol{B}}{\partial t}, && \text{(B.19)} \\ \mathrm{div}\,\boldsymbol{B} &= 0, & \mathrm{curl}\,\boldsymbol{B} &= \frac{1}{c^2}\frac{\partial \boldsymbol{E}}{\partial t}. && \text{(B.20)} \end{aligned}$$

If we have materials. we introduce two auxiliary fields, the *electric flux density* $\boldsymbol{D}$ and the *magnetic field strength* $\boldsymbol{H}$:

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P}, \;\; \boldsymbol{H} = \frac{1}{\mu_0}\boldsymbol{B} - \boldsymbol{M}. \tag{B.21}$$

Here, $\boldsymbol{P}$ is the *polarization* and $\boldsymbol{M}$is the *magnetization.* They must be determined from the bound charge density ρ_b and the bound current (localized loop currents) density $\boldsymbol{J}_b$ in the material:

$$\rho_b = -\mathrm{div}\,\boldsymbol{P} \tag{B.22}$$

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[113] following Landau-Lifshitz

and the macroscopic Maxwell's equation under the presence of material reads

$$\operatorname{div} \boldsymbol{D} = \rho_f, \qquad \operatorname{curl} \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}, \tag{B.23}$$

$$\operatorname{div} \boldsymbol{B} = 0, \qquad \operatorname{curl} \boldsymbol{H} = \boldsymbol{J}_f + \frac{\partial \boldsymbol{D}}{\partial t}, \tag{B.24}$$

where $\rho - \rho_b = \rho_f$ (the free charge density) and $\boldsymbol{J} - \boldsymbol{J}_b = \boldsymbol{J}_f$ (the free current density).

4 Preliminary III: Materials coordinates

4.1 Materials stage of thermodynamics

Usually, thermodynamics textbooks discuss internal energy E and work coordinates such as volume V to describe a system. However, these textbooks often overlook the materialistic basis of the system before introducing these thermodynamic coordinates. It is important to remember that even the ordinary thermodynamic coordinates E and $\boldsymbol{X}$ require materials to exist and be carried by them.[114]

Thus, we have already mentioned the material stage (→**3.9**). On this stage, the quantities E and $\boldsymbol{X}$ act as actors (→**3.9**), playing their roles in the thermodynamic processes.

However, the material stage of thermodynamics differs significantly from the ordinary stage for dramas, as it undergoes substantial changes when the actors perform their actions. These changes often cause trouble and complications. For instance, if there are variations in the quantities $(E, \boldsymbol{X})$, it leads to passive changes in the material composition of the system.[115] Even without any intervention from the experimenter, chemical changes are induced.

4.2 Conventional approaches with chemical reactions

Due to the trouble alluded in **4.1**, serious textbooks adopt one of two strategies to address this issue:

(1) To allow all chemical reactions to be halted at will, without disturbing the equilibrium state[116] (→**4.16**) or to be in a special metastable equilibrium known as frozen equilibrium[117].

(2) To acknowledge that chemical reactions exist in nonequilibrium states, while the ordinary thermodynamic coordinates E and $\boldsymbol{X}$ still adhere to the ordinary equilib-

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[114] The author calls this the *no ghost principle*. Even information requires its carrying material.

[115] In physics, where there is action, there is reaction. If the stage changes, actors would be strongly affected. However, in thermodynamics, there is a notable asymmetry. We can fix E and $\boldsymbol{X}$ from outside the system, in principle, even when the chemical composition of the system changes. We can fix the chemical composition with the aid of appropriate chemical reservoirs while altering E and $\boldsymbol{X}$. However, the maintained chemical composition is no more an equilibrium composition of the system with the modified E and $\boldsymbol{X}$. Instead, it is a nonequilibrium steady state. In general, we cannot fix the chemical composition while maintaining the system equilibrium.

[116] J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, 1961), p.100.

[117] E. A. Guggenheim, *Thermodynamics* (North-Holland, Fifth revised edition 1967), p.35.

rium thermodynamics[118].

Approach (2) is an eclectic strategy, and the consistency of its fundamental assumption, that only chemistry can be maintained in a non-equilibrium state without modifying ordinary equilibrium thermodynamics, raises concerns, so we will disregard this strategy.

Approach (1) may be more realistic if all reactions proceed very slowly; in such cases, a small amount of appropriate catalysts can be added to accelerate the reactions. However, it is worth noting that many reactions occur spontaneously at non-negligible rates. Negative catalysts can be proposed to inhibit such reactions, but this would require adding stoichiometric amounts of catalysts to the system. In short, approach (1) relies on unrealistic assumptions.

Therefore, in the present exposition, we will outline equilibrium thermodynamics without interfering with any natural chemical reactions in the system.

4.3 Elementary chemistry thermodynamics relies on

Here, elementary chemistry thermodynamics relies on is briefly summarized. Notice that it is provided by chemistry to thermodynamics; thermodynamics simply accepts it as a collection of empirical facts.

(i) The law of definite proportions: This law states that a chemical compound always contains its component elements in fixed ratio (by mass).[119]

(ii) Chemical reactions occur: The amounts of chemicals the experimenter adds to the system are generally different from the actual changes of the amounts in the system.

We accept at least the following three principles:

(I) Mixing and separating of chemical compounds are possible quasistatically and reversibly.

(II) Any mixture of chemicals eventually reaches a unique equilibrium composition for each $E, \boldsymbol{X}$.[120] In other words, a chemical equilibrium state is unique in the fol-

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[118] I. Prigogine and R. Defay, *Thermodynamique Chimique* (Editions Desoer, 1950).

[119] However, in, e.g., mineralogy or geochemistry nonstoichiometric compounds are not at all rare, so this law must be relaxed: in a given equilibrium state, the available compounds in the system must exhibit the definite composition (that may depend on E and $\boldsymbol{X}$, the ordinary thermodynamic coordinates).

[120] **On the uniqueness of chemical equilibrium** Even if the initial equilibrium state of a chemical system is clearly specified, the final equilibrium state attained through relaxing some internal constraints may not be unique, as non-quasistatic processes can occur. However, if the ordinary thermodynamic coordinates $(E, \boldsymbol{X})$ of the final state are specified, then the chemical

lowing sense:
For a *closed system* (= a system without any materials exchange with its environment), if moles of sufficiently many chemical compounds[121] to specify the material composition of the system are given, the current chemical composition is uniquely determined.
(III) Any chemical reaction[122] may be realized as an ionic reaction electrochemically. This fact is necessary to demonstrate (in principle) the equivalence of chemical and mechanical work.

4.4 What is a chemical reaction?

What is the essence of chemical reactions as physical phenomena? It is the change of the system chemical composition without any materials exchange between the system and its environment.

4.5 Trouble with expressions of amounts of chemicals

As is in (II) of **4.3**, for a closed system, if $(E, \boldsymbol{X})$, the set of all the ordinary thermodynamic coordinates (internal energy and work coordinates), is given, the moles of chemicals actually present in the system in equilibrium are uniquely determined. Generally speaking, if $(E, \boldsymbol{X})$ changes, the chemical equilibrium would shift. Therefore, even if we do not modify the system chemical composition $\tilde{\boldsymbol{N}}$ directly from outside the system, $\tilde{\boldsymbol{N}}$ changes. That is, the chemical composition variables $\tilde{\boldsymbol{N}} = \{\tilde{N}_i\}$ are not independent from $(E, \boldsymbol{X})$.

However, the ith compound may be added to the system independently of other chemicals. In this sense the variables expressing the moles of chemicals $\{N_i\}$ should

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composition of this final state is uniquely determined. This is the claim of (II).

The reader might argue that even if the final state (e.g., specified by T and P in typical lab experiments) is the same, the yield of a compound can vary significantly due to experimental procedures, much like cooking. Many reactions proceed very slowly, so this variation is simply a result of nonequilibrium effects. Furthermore, the compound you intend to synthesize may only exist as a metastable state.

As discussed in **2.5** about the nature of equilibrium states, sometimes we can ignore very slow reactions when studying the chemical thermodynamics of a system.

[121] For example, all the amounts of chemical compounds used to prepare the system materially at the start of an experiment

[122] Even a simple conformational change that does not require any chemical bond changes is a kind of chemical reaction. In such cases, no bond need be dissociated or reconnected, but still we can realize it through bond dissociation/reconnection processes.

be handled as independent variables. Still, we must not forget that even if we add δN_i moles of the ith chemical to the system, the amount of chemical i present in the system may not increase by δN_i.

For example, consider the following reaction:

$$\mathrm{A} + \mathrm{B} \longleftrightarrow \mathrm{C}. \qquad (*)$$

Chemicals A, B or C may be added to the system freely and separately by the experimenter, so the moles to express their amounts appear as independent variables. However, due to the chemical equilibrium, the actual amount of C present in the system is determined by the amounts of A and B in the system, so only two of A, B, and C are independent.[123]

4.6 Descriptions of experimental operations and of chemical composition of a system

4.5 tells us that there are two aspects for chemical quantities (moles of chemical compounds): (i) the operational aspect expressing the amounts of the chemicals the experimenter can add to the system, (ii) the descriptive aspect expressing the actual amounts of the chemicals in the system. Here, in case (i) all the amounts of chemicals may be understood as independently modifiable variables, but not so in case (ii).

4.7 Closed systems do not have independent variables describing amounts of chemicals

In particular, if the system is closed, there is no independent variable expressing the amount of chemicals.

Operationally in the sense of (i) in **4.6**, no such variable can exist, since no operation, i.e., adding or subtracting a chemical, is allowed; Descriptively in the sense of (ii) in **4.6**, although the amounts of compounds can change, e.g., by varying the internal energy, such changes are subordinate to or dependent on $(E, \boldsymbol{X})$, so there is no independent variable describing chemicals at all.

4.8 The moles of chemicals actually existing in the system are inconvenient thermodynamic variables

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[123] For a closed system with fixed $(E, \boldsymbol{X})$, the chemical equilibrium is definite. Consequently, as will be explained in **4.7**, there is absolutely no amounts of chemicals the experimenter can change at will.

Let us denote as $\tilde{N}_i$ the mole number of the ith chemical that is actually present in the system and that the experimenter can add to the system separately (independently) from other chemicals. We denote $\tilde{\boldsymbol{N}} = \{\tilde{N}_i\}$, collectively. If we know $\tilde{\boldsymbol{N}}$, the chemical composition of the equilibrium state of the system at present is completely known to us.[124] Let us call $\tilde{\boldsymbol{N}}$ as the *chemical composition* (variables or coordinates).

However, if we adopt chemical composition $\tilde{\boldsymbol{N}}$ to describe the materials stage of the system as a part of thermodynamic variables as the conventional textbooks, as already alluded above (→**4.1**), at least the following inconveniences follow:[125]
(i) The presence of chemical equilibria implies that $\tilde{N}_i$ are mutually related, so $\tilde{\boldsymbol{N}}$ cannot be a collection of independent variables.
(ii) Even if the system is closed, if E and $\boldsymbol{X}$ (i.e., the ordinary thermodynamic variables) are changed, usually, $\{\tilde{N}_i\}$ also change. That is, $\tilde{\boldsymbol{N}}$ cannot be independent of $(E, \boldsymbol{X})$.[126] In particular, if the system is closed, $\tilde{\boldsymbol{N}}$ are completely subordinate to $(E, \boldsymbol{X})$.
(iii) Even if the experimenter add $\delta\tilde{\boldsymbol{N}}$ to the system, usually, its composition is not given by $\tilde{\boldsymbol{N}} + \delta\tilde{\boldsymbol{N}}$.

Consequently, the chemical composition variables $\tilde{\boldsymbol{N}}$ that are adopted as the standard chemical variables by all the textbooks are at least very inconvenient and actually inadequate variables, if we avoid an artificial assumption that all the chemical reactions can be halted freely at any moment while keeping the system in equilibrium (→**4.2**).[127]

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[124] ⟪**Intrinsically accompanying compounds**⟫ Precisely speaking, not all the chemicals in the system can be operationally separately handled by the experimenter. In the usual chemical thermodynamics, the chemicals that the experimenter cannot regulate are ignored. A typical example is the chemicals that may be called 'intrinsically accompanying compounds' that always accompany a given chemical. For example, if we take an amount of liquid water, H_3O^+, $H_5O_2{}^+$, etc., come inevitably with it. Or if we take acetic acid gas, we cannot avoid dimers. The amounts of associated chemicals are fixed due to chemical equilibria (and very often their amounts are small), so we ignore these chemicals.

However, the composition of a 'pure chemical' changes due to, say, E, so the choice above is only an approximate procedure.

[125] The ordinary chemical thermodynamic textbooks assume, as noted in **4.2**, that all the chemical reactions can be freely halted at any moment as an equilibrium state. If we assume this artificial (and unrealizable) assumption, the following problems disappear. However, in this exposition of thermodynamics, we maximally avoid such an unnatural assumption.

[126] As can be guessed easily, $\tilde{\boldsymbol{N}}$ are partition additive but not additive quantity (→**2.13**).

[127] A dire consequence of this assumption is that the formulation of the second (law turns out to be difficult, if the law also governs chemical reactions.

4.9 Materials coordinates and chemical composition variables[128]

4.6 tells us that the variables (i) to describe experimental operations and the variables (ii) to describe the actual composition of the system must be distinct variables. Furthermore, **4.8** tells us that variables (ii) (chemical composition coordinates) $\tilde{\boldsymbol{N}}$ are disqualified as the basic independent thermodynamic coordinates.

Let us use the ordinary symbol N_i for the variable (i) to describe the chemical operation (collectively, $\boldsymbol{N} = \{N_i\}$). $\boldsymbol{N}$ denote the amounts of chemicals the experimenter prepares to make the system whose ordinary thermodynamic coordinates (i.e., internal energy and work coordinates) are $(E, \boldsymbol{X})$ and its chemical composition is $\tilde{\boldsymbol{N}}$. Let us call $\boldsymbol{N}$ the *materials coordinates* (or *chemical coordinates*).[129]

The chemical composition of the equilibrium state (specified by) $(E, \boldsymbol{X}, \boldsymbol{N})$ is uniquely fixed (→**4.3** (II)).

Notice that the materials coordinates $\boldsymbol{N}$ are additive.[130] For example, for the system whose work coordinate is only the volume V, if we prepare two copies with the states $(E, V, \boldsymbol{N})$ and $(E', V', \boldsymbol{N}')$ and combine them into a single system under a closed adiabatic condition, the resultant equilibrium state can be given by $(E+E', V+V', \boldsymbol{N}+\boldsymbol{N}')$. If the chemical compositions of $(E, V, \boldsymbol{N})$ are $\tilde{\boldsymbol{N}}$ and that of $(E', V', \boldsymbol{N}')$ $\tilde{\boldsymbol{N}}'$, the chemical compositions of $(E+E', V+V', \boldsymbol{N}+\boldsymbol{N}')$ are not necessarily $\tilde{\boldsymbol{N}} + \tilde{\boldsymbol{N}}'$.

4.10 A simple illustration exhibiting the non-additivity of chemical composition variables

Let us allow the exchange of chemicals between the two systems. For simplicity, the systems are assumed to have only one work coordinate V, which is fixed. As a reaction in the system

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[128] It is generally believed that the amounts of chemicals are not continuous, so '$d\boldsymbol{N}$' does not make sense. However, according to the macroscopic observation at our scales (→**1.4**) no discrete nature of the matter shows up. Even the law of constant compositions (→**4.3** (i)) does not logically imply the discrete nature of matter, even though this is a natural conclusion. Also note that we cannot ignore nonstoichiometric compounds. Therefore, in thermodynamics, the amounts of chemicals are modeled by an interval of reals $\mathbb{R}$.

[129] In order to construct a system with the state $(E, \boldsymbol{X}, \tilde{\boldsymbol{N}})$ the chemicals the experimenter must prepare are generally not unique. For example, if a system is with the reaction A + B $\longleftrightarrow$ C, we can appropriately mix all A, B, C, or only A and C to construct the same equilibrium state (see **25.5**, **25.6** for detail).

We can also choose $\boldsymbol{N}$ so that they numerically agree with the current composition $\tilde{\boldsymbol{N}}$. However, if we add $\delta\boldsymbol{N}$ moles to this system, the resultant state has its materials coordinates $\tilde{\boldsymbol{N}} + \delta\boldsymbol{N}$, but of course its chemical composition is, generally speaking, *not* $\tilde{\boldsymbol{N}} + \delta\boldsymbol{N}$ due to chemical reactions.

[130] This is due to the conservation of elements and the law of constant compositions, but does not logically imply atomism. This fact is imported from elementary chemistry to thermodynamics.

assume ($*$) in **4.5**. In systems I and II the reactions must be in equilibrium. Combining these two systems, the materials coordinates for the combined systems are simply the sum: ${N_{\mathrm{A}}}^{\mathrm{I}} + {N_{\mathrm{A}}}^{\mathrm{II}}$ and ${N_{\mathrm{B}}}^{\mathrm{I}} + {N_{\mathrm{B}}}^{\mathrm{II}}$ (and for C ${N_{\mathrm{C}}}^{\mathrm{I}} + {N_{\mathrm{C}}}^{\mathrm{II}}$).

What happens to chemical composition variables such as $\tilde{N}_{\mathrm{A}}$? As shown in the following calculation example, the chemical composition of the resultant system is not $\tilde{\boldsymbol{N}}^{\mathrm{I}} + \tilde{\boldsymbol{N}}^{\mathrm{II}}$, which is not an equilibrium state.

We rely on rudimentary chemistry. For the concentrations, there is a relation [C]/[A][B] $= K$, where [X] implies the molarity of chemical X. For systems I and II, let the concentrations (molarities) of chemicals be a, b, c and A, B, C (respectively, using obvious notations). Assume I and II have the same volume and temperatures. K does not change before and after the combination of the systems, so the question is: if $c/ab = K$ and $C/AB = K$, can the same hold for the average concentrations: $[(c+C)/2]/[(a+A)/2][(b+B)/2] = K$? Needless to say, this holds only for very special choices. If $K = 1$, $A = 3a$, $B = 3b$ and $C = 9c$ imply $[10/2]/[4/2][4/2] = 5/4 \neq 1$. Thus, $\tilde{N}_{\mathrm{A}}^{\mathrm{I}} + \tilde{N}_{\mathrm{A}}^{\mathrm{II}} \neq \tilde{N}_{\mathrm{A}}^{\mathrm{I+II}}$, etc.

4.11 The significance of materials coordinates

Since materials coordinates are not very explicit in the ordinary thermodynamics, let us summarize the significance of introducing such coordinates.

As seen in **4.9** the materials coordinates are additive, but chemical composition variables are not (although still partition additive →**2.13**).

The materials coordinates are individually independent variables and are also independent from the ordinary thermodynamic coordinates E and $\boldsymbol{X}$. If the experimenter adds $\delta\boldsymbol{N}$ moles of chemicals, then the materials coordinates of the system changes as $\boldsymbol{N} \to \boldsymbol{N} + \delta\boldsymbol{N}$. Note, however, in contrast to E or $\boldsymbol{X}$, the values of the materials coordinates do not immediately give the current chemical composition $\tilde{\boldsymbol{N}}$ of the system. The equilibrium composition $\tilde{\boldsymbol{N}}$ are given in terms of $\boldsymbol{N}$ only when the ordinary thermodynamic coordinates E and $\boldsymbol{X}$ are specified (→**4.12**).

4.12 Reaction map: $\boldsymbol{R}$

The relation between $\boldsymbol{N}$ and $\tilde{\boldsymbol{N}}$ may be described by the 'reaction map' R: R is the map that provides the equilibrium composition $\tilde{\boldsymbol{N}}$ for the system with the materials coordinates $\boldsymbol{N}$ when the ordinary thermodynamic coordinates are given by $(E, \boldsymbol{X})$: $R_{E,\boldsymbol{X}}(\boldsymbol{N}) = \tilde{\boldsymbol{N}}$.

If the experimenter adds $\delta\boldsymbol{N}$ moles of chemicals to the system (i.e., if the materials coordinates are changed as $\boldsymbol{N} \to \boldsymbol{N} + \delta\boldsymbol{N}$), $R_{E,\boldsymbol{X}}(\boldsymbol{N} + \delta\boldsymbol{N}) - R_{E,\boldsymbol{X}}(\boldsymbol{N})$ is the actual chemical composition change $\delta\tilde{\boldsymbol{N}}$ in the system.

If the system is closed, its materials coordinates $\boldsymbol{N}$ can be fixed, but its chemical composition variables $\tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\boldsymbol{N})$ depend on (actually, determined by) E and $\boldsymbol{X}$ and are not independent variables at all.

4.13 Materials coordinates and work

Following the ordinary work coordinates in **3.10**, for reversible and quasistatic processes the energy change associated with the process to change materials coordinates is expressed as the following form (*chemical form* or *mass form*)

$$\zeta = \sum \mu_i dN_i \tag{4.1}$$

analogous to (3.11). Here, μ_i is an intensive variable called the *chemical potential* of the chemical i.[131] When there is no change of work coordinates, for a reversible and quasistatic adiabatic process this form is exact, i.e., we can write $\zeta = dE$.

However, it is not obvious whether the materials coordinates may be treated just as the ordinary work coordinates in thermodynamics (→**4.5**-**4.11**). If they may be, this is an empirical fact, so the relevant facts should be mentioned. This is empirically established by electrochemistry (esp., emf due to Faraday and Joule) and the empirical equivalence of electric and mechanical energies.

4.14 Operational coordinates

If we do not distinguish electromagnetic and mechanical works and chemical works (the so-called mass action →**4.13**), they will be collectively called the *generalized work*. The work coordinates and materials coordinates will be collectively called *operational coordinates* (or generalized work coordinates) and written as Y_i (collectively $\boldsymbol{Y}$). The name is chosen because experimenters can vary them independently at their will, in principle. In particular, it should be noted that $\boldsymbol{Y}$ does not include chemical composition $\tilde{\boldsymbol{N}}$.

However, do not forget that work coordinates and materials coordinates have significant distinctions (see esp. **4.8** (iii)).

4.15 Reversible and adiabatic change of materials

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[131] There is an opinion that at the beginner level it is pedagogically advantageous to introduce the concept of chemical potential apart from thermodynamics [for example, G. Job and F. Herrmann, Chemical potential—a quantity in search of recognition, Eur. Phys. J., **27**, 353 (2006))]. A justification says that pressure, temperature, etc., may be introduced independent of thermodynamics. Of course for pressure this is all right, since P is a purely mechanical concept, but it is questionable as to T; its natural and proper introduction requires thermodynamics. Furthermore, chemical potential was initially introduced by Gibbs to thermodynamics, so the justification above may not be appealing, although its intuitive introduction as a quantity indicating the direction of changes involving chemicals may be pedagogically of some meaning.

To consider the chemical form ζ (4.1) we need quasistatic reversible and adiabatic changes of materials coordinates. Such changes are allowed due to the possibilities of reversible mixing/separating of chemicals and reversibility of chemical reactions (→**4.3**). The mechanical work-chemical work equivalence must have been self-evident for those who considered chemical reactions just as (classical) mechanical changes as Helmholtz (→**A.17**), but this is not any scientific proof of the equivalence.[132]

To define chemical potentials operationally, a cylinder with a piston closed by an appropriate semipermeable membrane is used (for more details →**17.5**). There are two potential problems here.

The first problem is the well-known realizability of semipermeable membranes (or selectively permeable membranes): it is only fictitious to assume a membrane that can segregate a selected chemical perfectly, so such a fancy device should be expelled from the theory.[133] However, a selective permeable membrane is a symbol to describe the reversible process (I) in **4.3**: mixing and separating chemicals can be realized reversibly; the separation process may use (appropriately idealized) reversible chromatography, fractionating column, etc.

The second problem is to realize exchange of finite amount of chemicals adiabatically. That is, whether $dE = \sum \mu_i dN_i$ can be realized. When the work coordinate is only V, the process is illustrated in Fig. 4.1. The procedure is not very simple, so we will not use this process. A practically meaningful cases are under constant temperature and pressure, so we will discuss the cases with these conditions later (→**17.5**).

Fig. 4.1 Adiabatic reversible addition of chemicals is possible, in principle.

The shade of red expresses the concentration of a particular chemical.

A: We assume that the total amount of chemical we wish to add to the system is known. The pure chemical is in the round container, which is enclosed by a diathermal wall that does not exchange

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[132] Bohr told Heisenberg as follows, "By 'stability' I mean that the same substances always have the same properties, that the same crystals recur, the same chemical compounds, etc. In other words, even after a host of changes due to external influences, an iron atom will always remain an iron atom, with exactly the same properties as before. This cannot be explained by the principles of classical mechanics, certainly not if the atom resembles a planetary system." (W. Heseinberg, *Physics and Beyond* (translated by A. J. Pomerans, Harper & Row, 1971) p40.). Compare this with Helmholtz' talk (→**A.17**).

[133] This complaint may sound reasonable for critical people, BUT compared with the 'standing assumption' in the standard chemical thermodynamics textbooks that chemical reactions may be stopped at our will without destroying the system equilibrium is a much more drastic and fancy assumption than this.

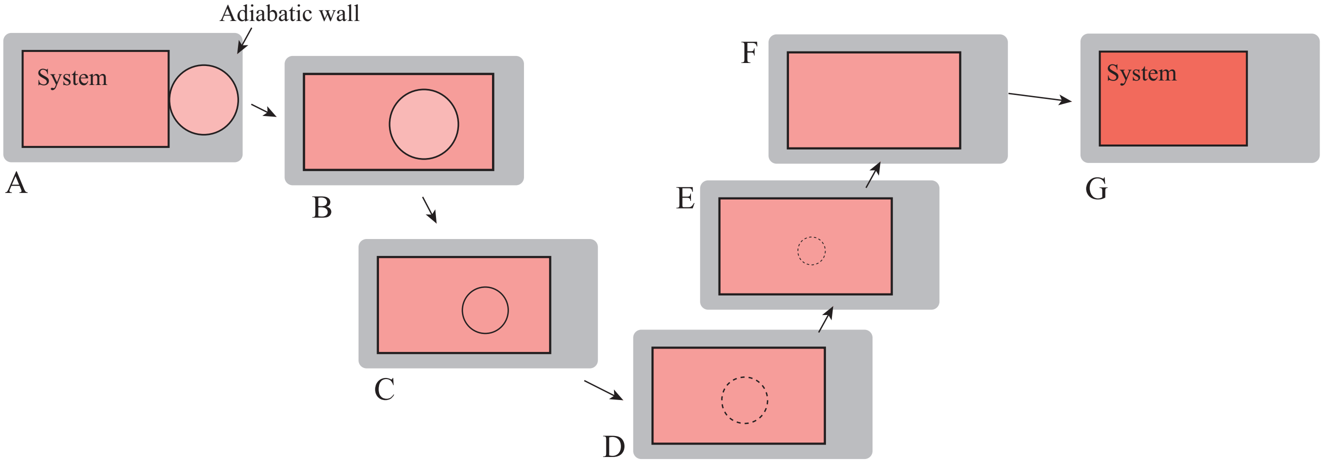

Figure 4.1: Adiabatic reversible addition of chemicals is possible, in principle.

any work coordinates (i.e., no displacement to change the container volume in the present case). Thus the total system is with a uniform temperature, and is enclosed by adiabatic walls.
B: We embed the container into the system. During this process we may choose the work coordinates, e.g., the volume, of the system quasistatically appropriately. Accordingly, E may change.
C: Regulate the volume of the round container appropriately to make the chemical potential inside and that of the same material in the system identiocal. E may change during this process.
D: Then, change the wall of the container with the selective permeable membrane for the target chemical.
E-F: Appropriately changing the volume of the round container and the work coordinate of the system we can squeeze out the chemical in the round container quasistatically.
G: Finally, the work coordinates are returned to the original values reversibly and quasistatically. Thus, without changing the work coordinates we have added the chemical reversibly and adiabatically.

4.16 Why no distinction between materials coordinates and chemical component variables appears in any textbooks

Perhaps this may be clearly understood from Kirkwood-Oppenheim's book or Tasaki's book. In short, the situations in which $\boldsymbol{N}$ and $\tilde{\boldsymbol{N}}$ must be distinguished are clearly avoided. That is, when chemicals are added (i.e., the operation by the experimenter), it is assumed that no chemical reactions are occurring at all. When chemical reactions occur and chemical compositions passively change even without direct material intervention by the experimenter, the system is considered closed. Therefore, in the former case we only need $\boldsymbol{N}$ and in the latter case only $\tilde{\boldsymbol{N}}$.

As is written in KO (p100):

> The application of the general criteria for equilibrium to systems in which chemical reactions may occur involves the ability to freeze the chemical reactions at any desired point. Thus, a system containing r substances which may undergo a chemical reaction must be considered to be made up of r independent components. At equilibrium, of course, the number of moles of any component is determined by specifying the number of moles of the $r-1$ other components and the values of the other pertinent thermodynamic parameters.

From this the equilibrium condition is obtained by a criterion of equilibrium under the restraint of closure: $(\delta E)_{S,V} \geq 0$.

The requirement for systems with chemical reactions is that "systems in which chemical reactions may occur involve the ability to freeze the chemical reactions at any desired point." While freezing reactions, the chemical coordinates are considered as our materials coordinates, and therefore, the convexity of E is preserved. As a result, as noted in the last paragraph, the usual thermodynamic variational principle for equilibrium states may be demonstrated.

However, with the conventional variables (corresponding to our chemical composition variables), if you turn on chemical reactions, the convexity of E is lost (→**4.10** for an example), so the validity of the usual thermodynamic variational principle for equilibrium states is no longer guaranteed. Consequently, the variational principle for chemical reactions cannot be established.

It is needless to say that the requirement to freeze reactions is quite unnatural; there is no device that can be conceived as an idealization of actual methods, as in the case of selective membranes.

Much more seriously, as we will see later, with the conventional material/chemical quantity expressions, the second law of thermodynamics with chemical reactions is hardly formalizable. Therefore, to put it bluntly, in the conventional approach the existence of entropy is not shown when chemical reactions occur.

Under the so-called Mechanical Weltanschauung, there is no problem, since chemistry is not considered special, as explained by Helmholtz (→**A.17**). Therefore, we can apply the second law with works alone, deeming it sufficient. However, 'Weltanschauung' is not science; lacking empirical basis, no matter how plausible it may sound. Thus, the conventional (or at least the original) formulation of chemical thermodynamics does not properly adhere to scientific moral code.

5 Preliminary IV: Thermodynamic space

5.1 Equilibrium states are distinguished by thermodynamic coordinates

Can we use the thermodynamic coordinates (→**3.9**) of a system to distinguish all the equilibrium states that we can macroscopically distinguish? Of course not. Note that, by definition (→**3.10**), thermodynamic coordinates cannot identify any changes that do not affect the internal energy, even if we can discern the change in the equilibrium state. For example, the difference in the three-dimensional shapes of the system or the relative positions of coexisting phases (say, ice and water) in it are irrelevant to thermodynamics.

Precisely speaking, a *thermodynamic state* (or *state*, for simplicity) is an equivalence class with respect to the thermodynamic coordinates of equilibrium states. Therefore, thermodynamics focuses on the changes of thermodynamic states rather than equilibrium states. From now on, however, we will not distinguish thermodynamic states and equilibrium states.

5.2 Thermodynamic space

The space spanned by the thermodynamic coordinates of a (simple[134]) system is called its *thermodynamic space*. The two equilibrium states that thermodynamics distinguishes correspond to two distinct points in this space (→**5.1**). Two equilibrium states whose thermodynamic coordinates agree are considered (thermodynamically) identical.

All thermodynamic coordinates may be measured in some energy unit,[135] so we may regard the thermodynamic space as the usual Euclidean space,[136] a metric space. We may regard it as the ordinary linear vector space with the usual metric. Thus, we can use the ordinary calculus in this space.

The thermodynamic space of a compound system is essentially the direct product of the thermodynamic spaces of the constituent simple subsystems.

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[134] This concept is not confined to simple systems. For a compound system its thermodynamic space may be the direct product of the thermodynamic spaces of the constituent simple systems or its convenient subspace.

[135] This is true even for materials coordinates

[136] Or, any vector space whose metric is equivalent to that of the ordinary Euclidean space.

5.3 Thermodynamic coordinates are privileged variables

For a given system its thermodynamic coordinates are the privileged coordinates with the following properties:
(1) They are extensive quantities that may be described and manipulated by non-thermal macrophysics and chemistry. In other words, thermodynamics is not needed to describe and to measure thermodynamic coordinates.
(2) They specify equilibrium states = thermodynamic states uniquely (by definition →**5.1**).

5.4 State quantity, state function

A physical quantity of a system is called a *state quantity*, if its value is fixed when the system is in a particular equilibrium state. That is, a quantity that can be described as a function (called a *state function*) whose domain is in the thermodynamic space is called a state quantity. A function of state functions is a state function. For example, temperature and pressure are not basic thermodynamic quantities (→**3.8**), but they are still state quantities. Therefore, their functions are state functions as well.

5.5 Thermodynamic densities and fields

The fundamental variables of thermodynamics are extensive variables (→**3.2**). Consequently, variables appearing in thermodynamics are extensive and intensive variables (→**3.2**). Also it was explained why theoreticians like to take the thermodynamic limit (→**2.14**), in which all the extensive quantities diverge and become meaningless. Therefore, to describe thermodynamics in this limit extensive quantities per unit volume, that is, the *thermodynamic densities* are used. Thus, in mathematical physics the key thermodynamic variables are the thermodynamic densities and their conjugate intensive variables (called *thermodynamic fields*).

The systems that we deal with at our scale (→**1.4**) are finite but they are typically very close to the thermodynamic limit; all the thermodynamic densities are virtually identical to their thermodynamic limit values.

In practice, it is often much more convenient to use the original extensive quantities rather than corresponding densities.[137] Therefore, in most cases, we will not use thermodynamic densities in the following expositions.

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[137] For example, changing only the system volume while keeping all other operational coordinates is not so easy to describe in terms of densities.

5.6 Let us study the topology of the totality of equilibrium states

The totality of the equilibrium states $\mathcal{E}$ of a system under study need not be the whole thermodynamic space (→**5.2**) of the system. If $\mathcal{E}$ is not simply connected (→**5.7**), then two paths connecting two different equilibrium states may not be continuously deformed into each other within $\mathcal{E}$, so the results of line integrals can depend on the paths taken. The following part of this section explains that the topology of $\mathcal{E}$ is ‘maximally’ simple and such ‘complications’ never occur.

5.7 Some topological terms[138]

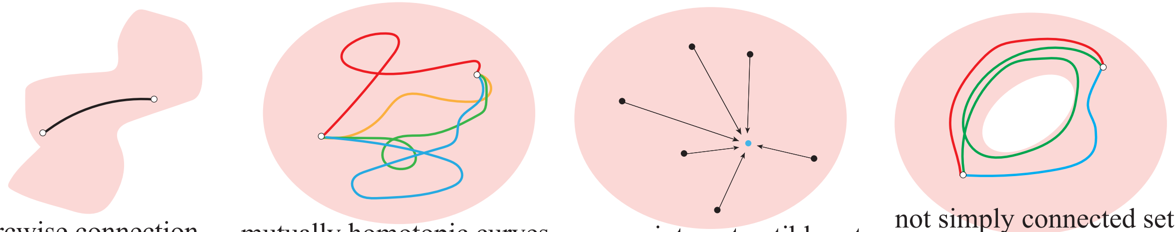
arcwise connection
mutually homotopic curves
one-point contractible set
not simply connected set; curves are not homotopic

Figure 5.1: Arcwise connection, homotopy, one point contractibility, simple connection

⟨⟨**Connected**⟩⟩ An open set is *connected*, if it cannot be divided into two disjoint open sets. A set is connected, if there is no way to cover it by two disjoint open sets that both have intersections with the set.
⟨⟨**Arcwise connected**⟩⟩ A set is *arcwise connected*, if any two points in the set may be connected by a continuous curve in it. Note that connectedness does not imply arcwise connectedness.
⟨⟨**Simply connected**⟩⟩ Suppose a set is arcwise connected and its any open set contains an arcwise connected open set.[139] If any closed continuous curve can be continuously contracted to a point in the set, we say the set is *simply connected*. Any closed continuous curve in a simply connected set is homotopic (see below) to a point.

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[138] A superb introductory book is: I. M. Singer and J. A. Thorpe, *Lecture notes on elementary topology and geometry* (Scott, Foreman and Company, Glenview, IL, 1967). Every student should read this.

[139] This condition says that the set is locally arcwise connected.

⟨⟨Homotopic⟩⟩ A continuous curve $f(t)$: $t \in [0,1] \mapsto \mathcal{E}$ is *homotopic* to another continuous curve $g(t)$: $t \in [0,1] \mapsto \mathcal{E}$, if there is a continuous map $F(t,s) : [0,1] \times [0,1] \mapsto \mathcal{E}$ dependent not only on t but one more parameter $s \in [0,1]$ such that $F(t,0) = f(t)$ and $F(t,1) = g(t)$. In short, if we can continuously deform the graph of f to that of g without leaving $\mathcal{E}$, we say f and g are homotopic.

⟨⟨One-point contractible⟩⟩ If a set S is homotopic to a point P in S, the set is said to be one-point contractible: that is, if we can construct a continuous function $F(x,t) : S \times [0,1] \mapsto S$ such that $F(x,0) = x$ and $F(x,1) = P \in S$, we say S is one-point contractible. In short, if we can continuously shrink a set to a point within the set, we say the set is one-point contractible.

5.8 Various equilibrium states

The concept of 'simple systems' was introduced earlier (→**2.9**) and it was stated that indefinitely complicated equilibrium systems may be conceived. Here, for simplicity, we assume all the simple systems are in spatially uniform equilibrium states.

If we prepare two simple systems and regard them jointly as a single system (Fig. 5.2A → B), even if there is no interaction between them, the resultant system is in equilibrium, since it satisfies the characterization of equilibrium states (→**2.7**). The resultant system is a compound system (→**2.9**).

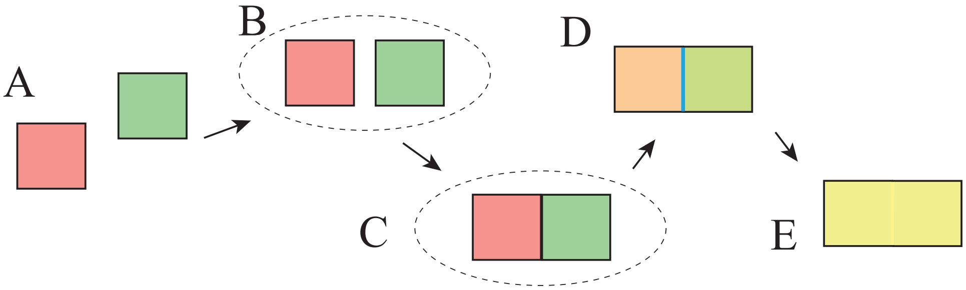

Figure 5.2: Various states of a compound system

Fig. 5.2 We can combine simple systems to make a compound system. The resultant compound system could be various, depending on the boundary conditions (walls) between the constituent simple systems.

A: Two simple systems in different equilibrium states.

B: It is of course possible to regard these simple systems as parts of a single system.

C: Even if these simple systems are connected through a wall that does not exchange any extensive quantities, there is no change of states from B.

D: Through varying the boundary conditions (i.e., wall properties →**2.1**), we can allow exchanges of some extensive quantities for a finite time span or forever to prepare various equilibrium states of a compound system.

E: We can further relax the constraints imposed by the wall; eventually, we could bring the compound system to a simple system (if both are made of the same materials).

As is illustrated in Fig. 5.2, by combining two simple systems, we can prepare various interpolative equilibrium states of a resultant compound system. Needless to say, we can start with as many simple systems as we wish, with walls of various types as we wish to separate them,[140] so we can make indefinitely complicated compound systems.

In thermodynamics, an inhomogeneous system may be understood as a compound system.[141]

5.9 $\mathscr{E}$ is a smoothly deformed convex set

Prepare two systems A and B. The thermodynamic coordinates of A are $\{E^{\mathrm{A}}, \boldsymbol{Y}^{\mathrm{A}}\}$ and those of B $\{E^{\mathrm{B}}, \boldsymbol{Y}^{\mathrm{B}}\}$, where $\boldsymbol{Y}$ denotes the operational coordinates (→**4.13**) $(\boldsymbol{X}, \boldsymbol{N})$. Grafting these two systems in certain proportions as illustrated in Fig. 5.3, we make a compound system. Then, we remove the wall, leaving the system to reach an equilibrium state.

As illustrated in Fig. 5.3, for any $\lambda \in [0, 1]$ we can make an interpolated system (this may not be a simple system) with its equilibrium state reached from the starting equilibrium state (of a compound system), whose total amount of the thermodynamic coordinates just before merging can be written as

$$\Lambda = (\lambda E^{\mathrm{A}} + (1-\lambda)E^{\mathrm{B}}, \lambda \boldsymbol{Y}^{\mathrm{A}} + (1-\lambda)\boldsymbol{Y}^{\mathrm{B}}). \tag{5.1}$$

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[140] ⟪**Requirement for walls**⟫ It should be fair to explicitly postulate that we can make a wall (prepare a boundary condition) between any systems that allows exchange of any set of extensive quantities (= operational coordinates→**4.13**) for any length of time.

The wall is assumed to have only local effects, except through the exchange of extensive quantities. If the reader knows phase transitions, she might question this, e.g., quoting Peierls' argument (for example, see Y. Oono, *Perspectives on Statistical Thermodynamics* (Cambridge, 2017) p419 and Q32.4 on p430). However, in this case the change in the order parameter has no energetic effect, so thermodynamically, we can ignore the effect (→**23.7**).

[141] As already noted (biological) 'cells' are sufficiently macroscopic. Remember that still no one imagined that we are made of cells. To regard spatially inhomogeneous macroscopic equilibrium systems as compound systems is sufficiently accurate.

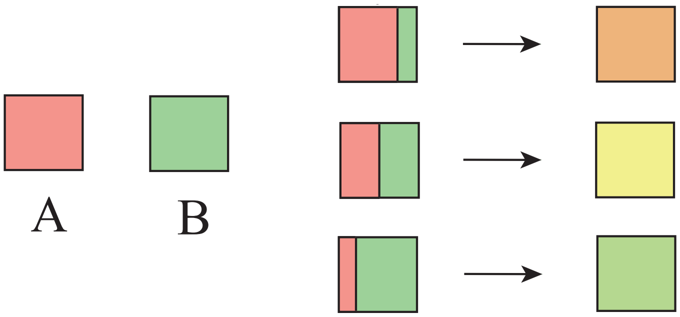

Figure 5.3: Making interpolated systems

If $\boldsymbol{Y}$ are additive (→**2.13**) (e.g., conserved) as E, then Λ itself denotes the thermodynamic coordinates of the resultant system. In this case if A and B are equilibrium states, then so is Λ: $\mathrm{A}, \mathrm{B} \in \mathcal{E} \Rightarrow \Lambda \in \mathcal{E}$. This implies that $\mathcal{E}$ is a convex set (→**5.10**).

This means that, since materials coordinates are all additive,[142] if all the work coordinates are also additive, then $\mathcal{E}$ is a convex set. However, the additivity is not guaranteed for all the work coordinates, so Λ may not be the thermodynamic coordinates of the final state. The true final equilibrium state 'C' $\{E^{\mathrm{C}}, \boldsymbol{Y}^{\mathrm{C}}\}$ is with $E^{\mathrm{C}} = \lambda E^{\mathrm{A}} + (1-\lambda)E^{\mathrm{B}}$. Its operational coordinates $\boldsymbol{Y}^{\mathrm{C}}$ must be a continuous function of $\lambda \boldsymbol{Y}^{\mathrm{A}} + (1-\lambda)\boldsymbol{Y}^{\mathrm{B}}$. Therefore, $\mathcal{E}$ may not be a convex set, but must be a set of a homeomorphic image of a convex set.

Consequently, any continuous curves connecting two particular points in $\mathcal{E}$ are homotopic (→**5.7**). Furthermore, $\mathcal{E}$ is one-point contractible (→**5.7**).

REMARK However, non-additive work coordinates are usually never discussed in the conventional thermodynamics.[143] Therefore **in this set of lectures, we assume that $\mathcal{E}$ is convex.**

5.10 Convex set

A set in a Euclidean space is a *convex set*, if the line segment connecting any two points in the set is in the set (Fig. 5.4).

any common set of two convex sets is a convex set.

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[142] Do not forget that the 'standard or conventional choice' adopted by all the textbooks, chemical compositions, $\tilde{\boldsymbol{N}}$, are *not* additive. However, this difficulty is evaded by the assumption that chemical reactions can be halted at any time as we wish.

[143] except for chemical composition variables $\tilde{\boldsymbol{N}}$ as the standard description of the amounts of chemicals.

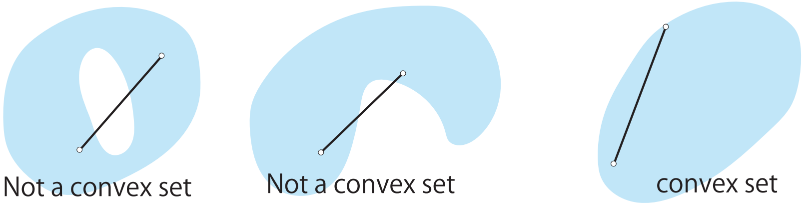

Figure 5.4: A convex set contains the line segment connecting two arbitrary points in the set.

The direct product of two convex sets is a convex set.

Thus, the totality $\mathcal{E}$ of equilibrium states of a given system is a convex set as we have seen in **5.9**).

5.11 Convexity and the choice of thermodynamic coordinates

As we have learned from the expression of chemical amounts in a system that are state variables, convexity of $\mathcal{E}$, the totality of the equilibrium states of the system, depends on the choice of the variables. This is stressed by Lieb and Yngvason on p33, "it is essential to note that the convex structure depends heavily on the choice of coordinates for" the thermodynamic space.[144] Thus, to cover chemical reactions thermodynamically, even within their 'axiomatic system,' how to describe amounts of chemical should have been discussed carefully.

5.12 Can we discuss the topology of $\mathcal{E}$ from partitioning of a system?

In **5.9** the nature of $\mathcal{E}$ was investigated through combining different equilibrium states. In contrast, Shimizu's Thermodynamics avoids 'dynamical changes due to making two systems in contact,' so he starts with Λ in **5.9**, so to speak, and then find its decomposition/partition into two simple systems. This is, in a certain sense, ingenious especially when the coordinates are not additive.

To be precise, let us quote the relevant statement from Shimizu's textbook: Theorem 4.2 contains the following statement: The entropy S of a system satisfies the following inequality for the sum of the entropies $S^{(i)}$ of simple subsystems that result from partitioning the system according to partition C

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[144] E. H. Lieb and J. Yngvason, "The physics and mathematics of the second law of thermodynamics," Phys. Rep. **310** 1 (1999). Incidentally, they wrote already on p7, "It is well known, as Gibbs (1928), Maxwell and others emphasized, that thermodynamics without convex functions may lead to unstable systems." "In our treatment it (= convexity) is essential for the description of simple systems."

($\{i\}$ denotes the pieces formed by partition C)

$$S(E, \boldsymbol{X}, C) \geq \sum_i S^{(i)}(E^{(i)}, \boldsymbol{X}^{(i)}).$$

Here, the *range* of $(E^{(i)}, \boldsymbol{X}^{(i)})$ is chosen to be additively consistent with $(E, \boldsymbol{X})$.

Comments on this statement follow:

(1) Here 'additive' must be interpreted as in the usual mathematics sense (not Shimizu's sense, i.e., 'partition additive' →**2.13**).

(2) Even if the word additive' is understood as in the standard mathematics, still the above statement needs the domain of the functions S (and $S^{(i)}$) specified. For example, the volume range may depend on the amount of the materials, so the 'range' is not simply determined by (the properly understood) additivity alone.[145] Thus, the range depends on $\mathcal{E}$. Then, the 'shape' of $\mathcal{E}$ cannot be determined by the additivity range alone.

(3) It is the other way around: $\mathcal{E}$ specifies the 'range' of the variables resulting from partitioning the original variables. Thus, even if $\mathcal{E}$ consists of two disjoint sets, we can choose the range of variables so that the partition satisfies the additivity.

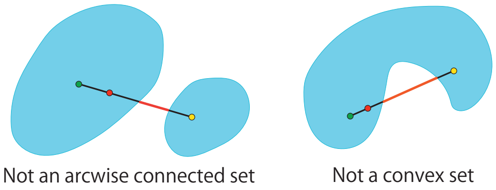

Figure 5.5: Additive constraints cannot determine whether $\mathcal{E}$ is convex or not. The red state may be the additivity consequence of the green and the yellow states. We can choose the ranges of these states even if $\mathcal{E}$ is not convex. If the green and the yellow states are given beforehand, Λ corresponds to any point on the segment connecting the green and the yellow states, so Λ may land on the 'orange' portion of the segment connecting the green and the yellow states. Thus, $\mathcal{E}$ must be a convex set.

Thus, the decomposability (or possibility of partitioning) of $(E, \boldsymbol{Y})$ does not properly impose any constraint on the topology of $\mathcal{E}$ [Actually, the decomposability is restricted by the geometry of $\mathcal{E}$]. See Fig. 5.5.

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[145] Generally, on the boundary $\partial\mathcal{E}$ the thermodynamic coordinates need not be independently changed. That is $\mathcal{E}$ need not be a direct product of intervals of the thermodynamic coordinates. Therefore, the domain of S must be given before discussing its additivity.

The convexity of $\mathcal{E}$ must be demonstrated separately from decomposability as we did (→**5.9**).

6 Preliminary V: Quasistatic processes

6.1 Points in the thermodynamic space

As we see in **5.3** any point $(E, \boldsymbol{Y})$ in the thermodynamic space of a system represents at most one equilibrium state (= thermodynamic state →**5.1**) of the system.

However, the coordinate values do not tell us whether the system is in equilibrium or not, so a point in the thermodynamic space may also correspond to some states of the same system with the identical $E, \boldsymbol{Y})$ but not in equilibrium. For example, for a single component gas, its thermodynamic coordinate system is (E, V). However, the energy and the volume can also be defined for non-equilibrium states, such as a swirling gas in a box. As a result, a process that can be described by a continuous curve in the thermodynamic space is not guaranteed to express a quasistatic and/or a reversible process.[146] If the system is a compound system, the situation can be more complicated.

In short, a process along which thermodynamics can be applied corresponds to a definite continuous curve in the thermodynamic space, but a continuous curve in the thermodynamics space need not represent processes to which thermodynamics can be applied.

To minimize confusion we introduce the concept of 'quasiequilibrium state' in this section.

6.2 Quasiequilibrium states: simple systems

The state P of a simple system (→**2.9**), whose thermodynamic coordinates are well defined (thus, it has a well-defined representative point P in the thermodynamic space), satisfying the following conditions, will be called a *quasiequilibrium state*:

(1) In a sufficiently small neighborhood of P is an equilibrium state R of the system,[147] and

(2) State P eventually reaches R, if the system is left alone in the single uniform environment $\mathcal{B}$ that can maintain R.

That is, the state P may not be an equilibrium state, but there is a true equilibrium state R sufficiently close to P, and if the system in state P is left in an

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[146] Needless to say, most nonequilibrium processes cannot even lie in the thermodynamic space.

[147] P can agree with R. That is, a point representing an equilibrium state can also represent a quasiequilibrium state.

environment that maintains R, the system eventually reaches R (Fig. 6.1).[148]

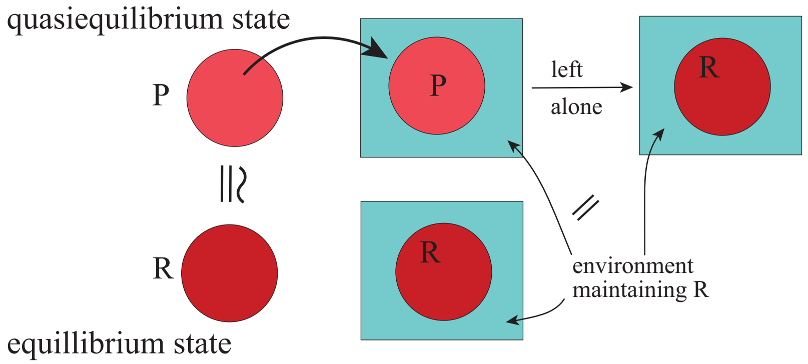

Figure 6.1: Quasiequilibrium state for simple systems

Suppose an irreversible change in a simple system is caused by a system-environment mismatch. For example, imagine a hot coffee in a thermos placed in a living room. If the thermos is of high quality, the state P of the coffee inside would be almost constant; if it is immersed in a heat bath $\mathcal{B}$ at approximately the same temperature, then it sooner or later reaches a true equilibrium state R, which is indistinguishable from P. That is, the state P is not a true equilibrium state, because it is cooling, but state P as a quasiequilibrium state is still located almost overlapping with equilibrium state R in the thermodynamic space. Thus, this state P is a quasiequilibrium state.

6.3 Quasiequilibrium states: compound systems

Since the case of general compound systems (→**2.9**) can be complicated, let us discuss a compound system consisting of two simple systems. If these simple systems are in quasiequilibrium states (→**6.2**) individually, the state P of the compound system corresponds to a point in its thermodynamic space (→**2.9**).

If we wish to say the compound system is in a ‘quasiequilibrium state,’ we must find a single uniform environment[149] $\mathcal{B}$ for the compound system such that the system in state P left alone in $\mathcal{B}$ eventually reaches an equilibrium state R of the compound system that is almost indistinguishable from P.

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[148] R can be P itself.

[149] Here, the environment must be a single uniform one, because, if we allow multiple environments, the subsystems of a given compound system can have its own environment and the whole compound system may be maintained in a nonequilibrium steady state.

An obvious problem is that combining two (quasi)equilibrium simple systems may not create a compound system in equilibrium. Suppose one simple system is hot water and the other cold water, and the boundary does not allow easy exchange of energy (i.e., informally, 'approximately thermally insulating'). If the combined system is in a good thermos, then far before the whole system reaches a room temperature, the system would relax to an almost thermal equilibrium at some common temperature. Even during the relaxation process the two simple systems can individually stay in quasiequilibrium states (at distinct temperatures), but there is no single uniform environment that can maintain this state of the compound system; as a state of a compound system, even though the change is slow, there is no equilibrium state close to the state.

A state represented by a point in the thermodynamic space, but without satisfying (1) of **6.2** may be called a *pseudoequilibrium state*.[150],[151] See the bottom of Fig. 6.2. The example in the preceding paragraph is a pseudoequilibrium state.

If one simple system is hot water, and if the other is also hot water of similar temperature, then, although the state P of the compound system is not in equilibrium, both simple systems are in quasiequilibrium, so P is in the thermodynamic space of the compound system. Furthermore, there is a (uniform) equilibrium state R sufficiently close to P. Therefore, P is a quasiequilibrium state of the compound system, satisfying (1) and (2) of **6.2**. In this example, if the whole system is in a thermos, and cools gradually, P is not a true equilibrium state of the compound system. Thus it is called a quasiequilibrium state. See Fig. 6.2Top.

6.4 Quasistatic process

If at every moment of the process the state of the system (irrespective of its inter-

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[150] When we discuss a compound system, note that the boundary conditions (walls) between subsystems are included in the definition of the compound system, so we do not touch them.

In the case being discussed here, if the wall between the simple systems totally isolates them, the state is a quasiequilibrium state, because there is an environment to keep it as an equilibrium state of a compound system (e.g., an adiabatic environment). As seen from this example, the magnitude of the relaxation times is the key. If the internal relaxation is quicker than that of the external relation, the system cannot be in a quasiequilibrium state, but a pseudoequilibrium state. In the opposite case, we may regard the state of the compound system as a quasiequilibrium state. Recall the characterization of equilibrium states by Feynman **2.5**.

[151] A pseudoequilibrium state is a state that changes quasistatically, but there is no single bath to maintain an equilibrium state very close to it. We can apply thermodynamics to the process consisting of pseudoequilibrium states, but the process is not generally reversible.

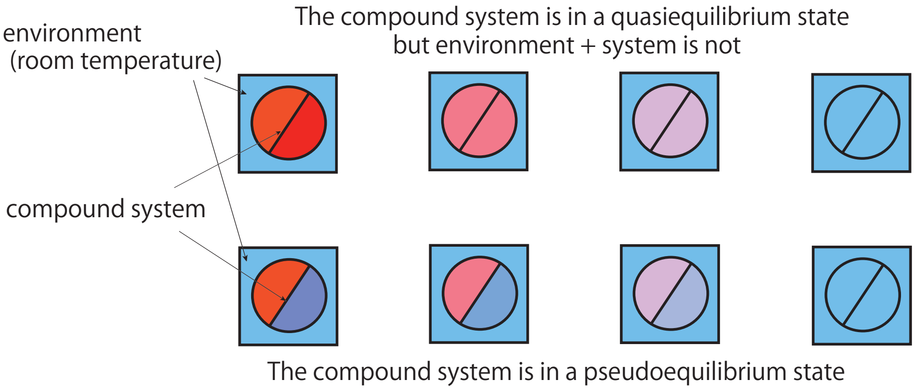

Figure 6.2: Quasi- and pseudoequilibirium states for compound system

acting exterior world—its environment, etc) is in a quasiequilibrium state (→**6.2**, **6.3**), we say the process is a quasistatic process.[152] Along a quasistatic process we can apply thermodynamics.[153]

Roughly speaking, when a system changes due to interactions with its environments, a process is a quasistatic process if any state along it can settle down to a very close equilibrium state if the system-environment interaction is severed.

By definition, the quasistatic process is about the system under consideration alone, because what matters is whether the system is always in quasiequilibrium states. Even if the system is interacting with something else, we do not care whether this other system is in (quasi)equilibrium or not. We also do not care whether the system is in equilibrium with it.

Informally speaking, at least for simple systems, if the process is sufficiently slow, it is a quasistatic process[154] for the system. For compound systems slowing down alone is not enough due to the possibility of pseudoequilibrium states (→**6.3**).[155]

Remark: Notice that a 'quasistatic process' is not simply a 'sufficiently slow pro-

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[152] **Warning**: The definition of 'quasistatic process' may vary depending on the source. Many books require that not only the system itself, but its environment are quasistatic in our sense and that the system and its environment must be in equilibrium. Then, they say that we can apply thermodynamics along quasistatic processes according to their definition. However, thermodynamics can be used under less strict conditions (e.g., no system-environment equilibrium is required (→**14.13**), the definition is not suitable for this purpose.

[153] Needless to say, if the initial and the final states are in equilibrium, we can always use thermodynamics to compute the state quantity evolution. Here, what is said is that along a quasistatic process at any point along the process we can use thermodynamics to compute the state quantities.

[154] This does not mean that the process is retraceable.

[155] Still, for individual subsystems we may use thermodynamics.

cess', distinct from Tasaki's explicit characterization. Historically, as can be seen in **A.6**, the chief motivation to introduce a quasistatic process was to avoid any loss/dissipation. Therefore, to equate being quasistatic and being slow does not correctly capture the connotation of the word 'quasistatic' in the original spirit.

6.5 'Physics' of quasistatic process

The idea of quasistatic process first appeared in the theory of hydraulic machines (→**A.6**). Carnot adopted this idea in his reversible engine as a process with changes at an infinitesimal rate (→**A.7**). The idea was readily accepted thanks to the popularity of analysis in France at that time.

Macroscopic observations are observations ignoring (or averaging-out) fluctuations that are spatially small and temporally rapid according to the law of large numbers. In other words, the observational errors of macroscopic observation occur only when the errors significantly exceed (standard) deviations of fluctuations. Even if we ignore fluctuations, they do not cease to exist, but in equilibrium there is no systematic deviation in one direction caused by equilibrium fluctuations (the average vanishes). However,[156] by nudging these fluctuations gently externally, the averages of fluctuations can be made nonzero.[157] Thus, quasistatic processes can be realized at rates sufficiently small but finite. The mathematical infinitesimal rate is a theoretical idealization of such small but finite rates.

In other words, deviations from the law of large numbers, i.e., the deviations theoretically understandable by the large deviation principle can, realize quasistatic processes.[158]

6.6 Reversible quasistatic processes

During a process of a system, if its environment is in a quasistatic state and if the compound system made of the system itself and its environment is also in a quasistatic state (→**6.3**), then the process is step-by-step retraceable, so it is reversible in particular.

6.7 Reversible process, quasistatic process and infinitesimal process

There is no direct logical relation among the concepts, 'reversible process,' 'quasistatic process,' and 'sufficiently slow infinitesimal process.' Here, some related remarks are collected.

(1) A quasistatic process is a process in which the system is in quasiequilibrium states

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[156] The discussion here essentially follows that of Koichi Ohno, *Learning Thermodynamics from Basics* (Iwanami 2001) p88 [In Japanese]

[157] This is the content of the so-called fluctuation-response relations in equilibrium statistical thermodynamics.

[158] Einstein's thermodynamic fluctuation theory exactly describes this large deviation theoretical framework as discussed in YO, *Perspectives on statistical thermodynamics* (Cambridge UP, 2017).

(→**6.2**). For work coordinates, if there is no 'dry friction,' such a process is realizable by sufficiently slowing down the changing rates (→**3.11**). Materials coordinates may be handled basically in the same fashion as the work coordinates, although some care is required. For heat see **14.12**.
(2) Even if the changing rate of operational coordinates or their conjugate variables is small, the change need not be reversible. It is possible to realize the situation analogous to the slowly cooling cup of coffee for work coordinates. A gas container with a pinhole is an example. For the gas in the container of volume V, its state, e.g., its pressure P, is almost constant. However, for the portion of the gas leaking from the hole, its volume expands very quickly from a tiny one to 'the whole world.'

Very similar to this, we could connect two containers containing gases of different pressures, respectively, with a small pin hole. Each container is in a quasiequilibrium state, so each container changes quasistatically. However, the whole system is not in equilibrium (not even in a pseudoequilibrium state →**6.3**). This is an example of irreversible changes of a compound system consisting of simple systems undergoing quasistatic changes.

It is easy to make such a counterexample for chemical reactions with the aid of the so-called negative catalysts that can indefinitely slow down chosen reactions.
(3) However small a change relative to the whole system, if the change itself is violent (not controllable), then even though the change is quasistatic for the system and may be infinitesimal, it may not be reversible. It may be easy to imagine such a situation with a gun powder ignited in small portions. Suppose a container of gas is with a piston, and its outside is a vacuum. If the piston is pulled out stepwisely very rapidly as $V \to V + dV \to V + 2dV \to \cdots$, then each step is a free expansion of the gas, so is irreversible. That is, even if the change as a whole (from the point of view of the whole system) is 'slow' and infinitesimal, it is irreversible.[159]

6.8 Why is thermodynamics useful?

Thermodynamics discusses only equilibrium states, even though this world is full of nonequilibrium phenomena. Why is thermodynamics still useful? Because:
(i) Equilibrium states do not depend how they are prepared (→**2.7**).
(ii) Equilibrium states may be realized with good approximation.

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[159] In this case, the gas is always in a quasiequilibrium stateand so is its environment, but there is no (near) equilibrium relation between the system and its environment. That is why the process is not reversible.

In particular, the starting state S of a process is very often a time independent state, and so is the destination state F. Therefore, often it is not a bad approximation to regard these states as equilibrium states; the changes of state quantities (→**5.4**) are completely determined by the thermodynamic coordinates of these two states.

To compute the change of state quantities without knowing the actual process from S to F, we have only to devise a convenient curve in the (operational) thermodynamic space connecting S and F. The process described by the curve can be realized as a quasistatic reversible process (→**C.5**). A simple example is in **11.13**.

7 ‘The first law’ of thermodynamics

7.1 Sign convention

When energy is added to the system in the ordinary sense of the word (that is, not in an algebraic sense), such as, when the external world does work on the system, we say that the system receives a positive (+) amount of energy. If the system does work on its surroundings, we say the system receives a negative (−) amount of energy.

From now on, for any extensive quantity, if the system gains the quantity in the ordinary sense of the word, we assume a positive (+) amount of the quantity enters the system. If the system loses the quantity in the ordinary sense of the word, we say a negative (−) amount of the quantity enters the system.

In other words, our algebraic sign convention is based on a system-centered point of view. [Note that this sign convention is the opposite of Clausius’ convention for his equivalents (→**A.11**).]

7.2 The so-called ‘first law of thermodynamics’

As stated in **A.9** the works of Mayer and Joule led to the recognition that the law of conservation of energy applies to energies beyond mechanical energy; specifically, the sum of (correctly converted) ‘heat’ Q and (generalized) work W (→**4.13**) is conserved as energy. That is, the increase of the system energy ΔE may be written as $\Delta E = Q + W$. This relation has long been referred to as the first law of thermodynamics. Given the tradition of quantitative heat theory preceding Mayer’s and Joule’s works (→**A.2**), it was sensible to summarize the law of conservation of energy in this form.

Within non-thermal macrophysics, energy is a well-defined quantity in electromagnetism and mechanics, and so is work. In contrast, if ‘heat’ is to be quantitated independent of physics, as seen in **A.2**, we need ‘temperature.’ However, if we question what temperature is, its relation to the non-thermal macrophysics is quite opaque.[160]

Thus, ‘heat’ remains a mysterious concept in macrophysics unless it is directly

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[160] Needless to say, to understand thermal properties of gases, the kinetic theory of gases was devised according to classical mechanics. It directly connected temperature and kinetic energy, and certainly encouraged the mechanical Weltanschauung (→**1.3**). Still, such ‘speculations’ cannot be used to establish temperature within macrophysics.

related to work.[161]

The measurement of work W is already established in non-thermal macrophysics (→**3.11**). Therefore, the most direct way to define 'heat' is as $\Delta E - W$, provided a means of measuring ΔE is established.

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[161] That temperature is a measure of extent of molecular motion is not only a meaningless explanation macroscopically, but also not conceptually correct. Quantum mechanically, temperature is not exactly the extent of molecular motion.

⟪How fundamental is scalar temperature as a concept?⟫

Since thermodynamics must be based on macroscopic empirical facts (recall our basic discussions **1.5-1.8**), if you wish to construct thermodynamics in terms of the concept directly related to temperature (e.g., 'isothermy'), we must be able to establish the concept purely empirically without thermodynamics and nonempirical assumptions/particular Weltanschauungs.

We believe that 'temperature' is considered a scalar quantity nowadays, but it is highly questionable whether this belief is purely empirical. In contrast to pairs like short-long or light-heavy, we have at least two temperature-related pairs: cool-warm and cold-hot. These pairs correspond to biologically distinct mechanisms for sensing sensations such as warmth and heat. It is also important to note that sensors for hot and cold are different. In summary, the biological temperature 'scale' is a combination of distinctly sensed quantities, making it difficult to argue for a purely empirical basis for a scalar measure of temperature-related quantities. This distinction is quite different from the concept of length or weight (force).

We use words and concepts to describe something that exists outside the realm of concepts/ideas. No matter how many words and sophisticated mathematical concepts we accumulate, the connection between a concept and the actual entity cannot be uniquely established. Only if we have a "God-given" (innate) connection between the actual entity and the signals in our nervous system, can we unambiguously employ the concept/idea in empirical science. For instance, the force sensor is a calcium channel that converts molecular deformation into ion flux. Temperature, on the other hand, lacks such a clear biological mechanism, making it inherently ambiguous.

Then, why do we assume that there is a linear scale of temperature? The author strongly suspects that there are a few non-empirical components to our understanding of temperature. Initially, it was associated with the movement of the 'fire particle' and other concepts related to alchemy. These notions naturally became connected to kinetic theories influenced by the mechanical Weltanschuung. Naturally, the latter directly supported the establishment of the first law, as Helmholtz did (→**A.17**). Eventually, the concept of temperature as a scalar quantity was solidified by the contributions of Carnot, Clapeyron, and Thomson, and was finally defined in terms of entropy (→**11.6**).

When was 'temperature' really empirically established as a scalar quantity? The author suspects that it was only after the second law, which is unequivocally empirical. This suggests that using the notion of temperature or related concepts like isothermy to establish thermodynamics, as often done in elementary introductions, is logically circular.

One might propose that by assuming the usual empirical temperature as a scalar quantity and then constructing thermodynamics to demonstrate the possibility of defining thermodynamic temperature. However, this argument can be considered, at best, a self-consistency argument, which is not sufficient for establishing a fundamental theoretical framework.

7.3 Energetic equivalence of work coordinates and materials coordinates

The energy change due to any chemical reaction can, in principle, be converted reversibly and quasistatically to electrical energy.[162] Any reaction, including biochemical reactions, may be understood as a redox reaction, that is, the exchange of electrons. According to Faraday's law of electrolysis[163] and the fact that reversible cells can convert chemical energy to electrical energy qV reversibly, where q is the charge involved in the reaction and V the electromotive force of the cell.

Here, 'in principle' is added to the statement, because devising a reversible cell is not always simple. This applies to any chemical reaction; realizing reactions in principle possible is usually hard, particularly if the reactions are interesting and practically important.

7.4 Generalized work done by the external systems to the system

For thermodynamics how to compute generalized work forms (→**3.10** and **4.13**) for reversible quasistatic processes is dictated by non-thermal macrophysics and chemistry.

Ordinary macroscopic machines are designed to perform macroscopic work with high efficiency even at considerable speeds.[164] The work form may be computed according to the conventional macrophysics as illustrated in Appendix B after Section 4 (**B.1**, etc.).[165,166]

The energy change due to chemical changes (→**4.13**), the so-called mass action, may be reversibly converted to electrical work, so there is no new conceptual problem

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[162] Usually no such general argument is stated, but in essence, if all the chemical reactions may be realized as ionic reactions, this is possible (→**4.3**III).

[163] In a modern expression, we may say, "The amount of charge going through the reactor and the extent of reaction is proportional."

[164] For example, electric motors and dynamos are said to function at about 90% efficiency (mechanical energy ↔ electric energy). It is said if superconductors are used, about 10% efficiency increase is possible.

[165] This does not require that a complete theory for a particular work to be known. What is required is that the relevant work coordinate (extensive quantity) is operationally definable, and that the change of energy without dissipation due to the coordinate modification may be measurable (e.g., we can make a table of the conjugate variable empirically).

[166] Using a lossless generator or motor mechanical potential energy may be reversibly converted to various forms of work, so ΔE based on (3.11) may be written as Mgh in terms of some mass M and a vertical displacement h, where g is the acceleration of gravity. Therefore, by measuring h, the (generalized) work done to the system by the external system can be, in principle, measured.

(→**7.3**).[167]

Thus, the generalized work done by the external systems to the system can be measured.

7.5 Energy change and work coordinate changes of the system

Even if the (generalized) work, whose amount is ΔE, is done on the system as described in **7.4**, there is no guarantee that the (generalized) work done by the external system was converted to reversible changes of operational coordinates (→**4.13**) of the system. A portion of the added external work ΔE may be dissipated inside the system, converted to 'heat.' Nevertheless, we can measure how operational coordinates of the system have been changed, and the total energy ΔE added to the system is also known. Therefore, if the thermodynamic coordinates of the initial equilibrium state are known, those for the final equilibrium state can also be known.

7.6 Necessity of adiabatic environment[168]

During the process described in **7.4**, the generated 'heat' should not leave the system, nor 'heat' should enter the system from outside. When the added generalized work ΔE (as described in **7.4**) is definite, the final energy of the system must also be increased by ΔE during the experiment. Furthermore, whether such a condition (henceforth called an *adiabatic condition* →**7.7**) is met or not must be verifiable experimentally.[169] The environment where an adiabatic condition is met is called an *adiabatic environment*.

7.7 Adiabatic condition, adiabatic process

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[167] Experimentalists took this fact for granted as seen in **A.16**, and theoreticians also did not seem to have any question about it as seen in Helmholtz's exposition (→**A.17**) and in Gibbs' basic thermodynamic paper quoted in **11.9**.

[168] There is an approach to define adiabaticity and energy conservation simultaneously (e.g., Tasaki defines energy through adiabatic work). However, energy was originally defined and its conservation law was established in mechanics (and is the backbone of mechanical Weltanschauung). No concept of adiabaticity is needed for the definition of mechanical energy. The concept of adiabaticity was required when we attempt to go beyond pure mechanics. Therefore, here, in line with our basic policy **1.8**, we presuppose energy before adiabaticity.

[169] These lecture notes focus more on the experimental verifiability of concepts and the measurability of various quantities than ordinary thermodynamics textbooks. This is in response to operational criticisms made by Glenn Paquette.

A wall is called an *adiabatic wall*, if the total generalized work required for a system in this environment from any initial equilibrium state A to any final equilibrium state B depends only on A and B and not on the actual process connecting them.[170]

Here, other than fixing A and B, whether the process is reversible or quasistatic or not does not matter. ΔE agrees with the energy the external systems loses.During the process the generalized work may be dissipated in the system. However, if the process is reversible and quasistatic, then integrating $\omega + \zeta$ (the general work form for quasistatic processes (4.1), (3.11)), we can obtain ΔE.

7.8 Adiabatic wall allowing no materials exchange

We may define adiabatic walls as in **7.7**, but to do physics the definition must be operational. That is, we must be able to check experimentally that 'the total sum of the generalized work is constant.'

Let us consider a wall that does not allow any exchange of matter. Let us check whether this wall is adiabatic. To this end we consider a closed system enclosed by the wall just specified. The thermodynamic coordinates of such a system consist of internal energy E and work coordinates $\boldsymbol{X}$. We further assume that the system has an 'energy meter property' (→**7.9**).[171] Then, we can always determine ΔE for the system by observing conjugate variables of the work coordinates. Therefore, in principle, we can experimentally check whether the wall is adiabatic or not.

7.9 Energy meter property

Let us say that a system has an *energy meter property*, if its intensive conjugate variables $\boldsymbol{y}$ of its operational coordinates $\boldsymbol{Y}$ depend on internal energy (density) injectively under fixed $\boldsymbol{Y}$ (more precisely, their densities).[172]

For example, all the thermometers are energy meters, that is, have an energy meter property; the so-called gas thermometer has the pressure that depends monotonically on the energy density under constant volume, so it is an energy meter.[173]As

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[170] Here, it should be emphasized that the work may be added irreversibly, or in whatever modes the work may be added. For reversible-quasistatic isothermal processes, the work form becomes exact (→**18.1**), but note that this is possible only for reversible processes.

[171] This is always possible, since there are systems that have the energy meter property. Besides, no system is known that lacks the energy meter property.

[172] That is, if $\boldsymbol{y}(E, \boldsymbol{Y}) \neq \boldsymbol{y}(E', \boldsymbol{Y}) \Rightarrow E \neq E'$.

[173] The reader may think that the energy meter property is more conveniently defined by the difference in $\boldsymbol{Y}$ under constant $\boldsymbol{y}$. Here, $\boldsymbol{y}$ are not fundamental variables and, as we will see later,

in this example, all the conjugate variables of operational thermodynamic coordinates are defined and measured within non-thermal macrophysics and chemistry, so we can measure them without knowing thermodynamics. In particular, whether ΔE is identical or not can be observed.

Just as not all the materials can make thermometers, there is no guarantee that all the materials/systems have an energy meter property. However, no example are currently known to lack this property.

7.10 Non-adiabatic environment

If the system can exchange energy with its environment even without exchange of generalized work, the environment is not adiabatic. The energy exchange without any generalized work in a non-adiabatic environment is called 'heat'; more precisely, if energy transfer is possible without any generalized work, we say energy is transferred as *heat*. In other words, if the total energy change is not solely due to generalized work, the discrepancy is said to be due to heat exchange.

Note that 'heat' is a mode of exchanging energy. It is not that something called 'heat' flows in or out (in contradistinction to 'caloric' →**A.2**). The energy entering a system as 'heat' and that as generalized work lose their distinction inside the system.

7.11 Quantitating 'heat'

How can we measure the energy exchanged as heat?

Suppose a system enclosed in a wall goes from its initial equilibrium state $(E, \boldsymbol{Y})$ to a final equilibrium state $(E + \Delta E, \boldsymbol{Y}')$ through performing generalized work $\tilde{W}$ on the system. $\Delta E - \tilde{W} = Q$ is the amount of heat the system exchanged with its environment. $\tilde{W}$ is measurable, because it can be supplied by mechanisms that can be realized quasistatically (→**7.4**).[174]

Thus, for 'heat' Q to be operationally defined, the problem is how to measure ΔE. If the system is an energy meter (→**7.9**), measuring conjugate variables, we can determine ΔE.

$\partial y_i/\partial Y_i$ is never negative (→**22.9**), so the condition: $\boldsymbol{y}(E, \boldsymbol{Y}) \neq \boldsymbol{y}(E', \boldsymbol{Y}) \Rightarrow E \neq E'$ is adopted as the characterization of the energy meter property.

[174] 'Quasistatically' for the environment or the external devices to supply work; this does not necessarily mean that the process is quasistatic for the system itself.

7.12 Thermal contact

A contact between two systems that is not adiabatic and does not allow exchange of any operational coordinates (→**4.13**) is called *thermal contact*. Suppose two systems are in thermal contact but are isolated as a whole. After a long time the whole system (generally as a compound system) would reach an equilibrium state. We say the two systems reach a *thermal equilibrium*.[175] What happens during the thermal contact is that one system loses energy Q as heat, and the other gains energy Q as heat. This Q may be measured as explained in **7.11**.

7.13 Are work and heat always distinguishable?

Up to this point all the statements have assumed that, as a mode to transfer energy, heat and work can always be distinguished, but this is not always true. If the change of a state is violent, then the spatiotemporal scale of the system state inhomogeneity could range from microscopic to macroscopic, making the distinction between heat and work ambiguous. However, in thermodynamics, we assume the distinction is clear, or, we discuss only 'slow' changes with the clear distinction between work and heat.

Here, 'distinction' means that heat and work may be distinguished as different modes of transferring energy. Once inside the system, the distinction is lost. It was once thought that heat was a flow of a special element called 'caloric,' so even after energy transfer as heat 'caloric' remained in the system. However, the idea lost popularity after Mayer and Joule (→**A.9**), especially after Joule's detailed experiments demonstrated convincingly that heat and work quantitatively interchange.

However, if the heat-work conversion does not happen, the total amount of heat a system exchanges with its environment is conserved, so heat treated as a conserved quantity (just as thought in the caloric theory) is still effective (as Black originally assumed →**A.2**).

7.14 Conservation of energy in thermodynamics

The quantitative definition of heat in **7.11** determines Q to satisfy the conservation of energy. Therefore, the so-called first law of thermodynamics $\Delta E = W + Q$ is no longer considered as a law of physics.

So, what is the core empirical fact intrinsic to thermodynamics? It is the principle

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[175] Notice that this does not mean that the two systems are in equilibrium under any contact; they are in equilibrium only with respect to the exchange of heat.

to be called the *Mayer-Joule principle* (→**A.9**): "Work can always be converted to heat at a definite conversion ratio." Chemical work is a type of work (→**4.13**). The generated heat can be added to any system, so the Mayer-Joule principle should read precisely as:

> Generalized work can be converted to heat at a universal constant conversion rate and added to any system.

The law of conservation of energy incorporating this principle is the so-called 'first law of thermodynamics.'[176]

In summary:

(i) Using generalized work (→**7.4**) and adiabatic processes (→**7.7**), the change of internal energy can be measured (→**7.9**). And

(ii) If the process is not adiabatic, the change of internal energy and the net generalized work added to the system can be different, and the discrepancy is defined as 'the energy transfer as heat' (→**7.11**).

(iii) Generalized work may always be converted to heat with a definite conversion rate (the Mayer-Joule principle), and

(iv) (ii) and (iii) are consistent with the law of conservation of energy of the nonthermal macrophysics and chemistry.

7.15 Comparison of mechanical energy and thermal energy

Suppose a mass of 1 kg is running at speed 100 km/h. Its kinetic energy is 386 J. If this mass is water and is heated with the thermal energy obtained by converting this kinetic energy, its temperature will not increase even by 0.1 K (actually about 0.092 K). This illustrates how thermal energy is 'much greater' than 'macroscopic mechanical energy.' Therefore, even the utilization of a 'tiny amount' of thermal energy can produce huge amount of work. This tells us how heat engine was revolutionary for humankind.

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[176] However, in thermodynamics, we wish to restrict the number of coordinates as few as possible, so violent changes must be avoided.

8 The second law of thermodynamics

8.1 The second law of thermodynamics: preliminary

Clausius' work (→**A.10**) demonstrating Carnot's theorem (→**A.8**) in a consistent fashion with the Mayer-Joule principle (→**A.9**) clearly established that 'heat' is a unique mode of energy transfer. Clausius' logical core, in his own words, goes 'through basically the same line of thought': if we deny Carnot's theorem, then we would have to accept a process that is highly improbable in reality.

Today, we demand that "a process highly improbable in reality" never happens as a principle called the *second law of thermodynamics*. As we will see below, there are various forms of the principle, but all are equivalent.[177]

8.2 The second law must explicitly consider materials coordinates as well

The ordinary electromagnetic and mechanical work may be reversibly and quasistatically converted to chemical energy through electrochemistry. This is possible due to Faraday's law of electrolysis and the existence of reversible electric cells (→**A.16**, **??**).

Consequently, there is no difficulty of principle nature to extend the first and the second laws of thermodynamics to handle materials coordinates (→**4.13**). Needless to say, however, the laws must clearly include chemistry as well.

There are two important points to pay special attention:

(1) The usual statement of the principles does not particularly quote any relevant empirical facts, but do not forget that the relation between the ordinary work and chemical work mentioned above requires empirical support.

(2) We must not forget the peculiar nature of chemical coordinates (→**4.9**, **4.11**).

8.3 Clausius' principle

When two systems are in (any) thermal contact (→**7.12**), very often one system always loses internal energy as heat, while the other always gains internal energy as heat.[178] The system losing energy is called a *hotter system* and the other a *colder system*. Recall that we can measure the amount of heat a system gains (→**7.11**).

Clausius' principle may be stated as:

> "It is impossible to transfer energy as heat from a colder system to a hotter system without leaving any trace in the surrounding world (environment)."

In thermodynamics what is not forbidden by its principles may happen (→**8.4**).

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[177] If not, what would happen? As long as all the natural phenomena are related, we would be able to violate (or overcome) the second law.

[178] The reason why 'always' appears here is that when a pair of systems are brought into thermal contact with each other, the hotter one is always hotter and the colder one colder. That is, the hotter-colder relation is solely determined by the individual states of the two systems. Note that the concepts 'hotter' and 'colder' are, at present, not related to any kind of temperature.

Thus, “It is allowed to transfer energy as heat from a hotter system to a colder system without leaving any trace in the surrounding world (environment).” Needless to say, “It is possible to transfer energy as heat from a colder system to a hotter system with some trace left in the surrounding world (environment).”

8.4 Metaprinciple of thermodynamics

In **8.3** is a rather strong statement, “anything that is not forbidden by its principles may happen,” but since no exception to this statement is known, we should accept this statement as an empirical principle about all the principles of thermodynamics. Therefore, we demand *metapriciple of thermodynamics*:

> “Negation of anything that thermodynamic principles explicitly forbids is allowed.”

Here, It is important not to ignore the word “explicitly” in the metaprinciple to prevent any misuse of the principle.[179]

8.5 Planck’s principle

Planck’s principle is conventionally stated as:

> If work coordinates do not change before and after the adiabatic process, the system internal energy cannot decrease.

However, there is no reason to exclude materials coordinates, so the law is revised as follows:

> If operational coordinates (→**4.14**) do not change before and after the adiabatic process, the system internal energy cannot decrease.

As stated in **4.9**, note that this does not fix the chemical composition of the system. In fact, if work coordinates return to the original values, and if chemical composition also returns to the original one, the system internal energy cannot change, so this principle loses its meaning. Note further that the system need not be closed

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[179] For example, while thermodynamics does not address anything about nonequilibrium phenomena, it should not imply anything allowed can happen in nonequilibrium. Therefore, even if the usual thermodynamic principles do not say anything about the relation between W (work) and Z (mass action →**17.1**), the metaprinciple does not imply that there is no constraint between the mutual conversion of them, since nothing is explicitly forbidden in this case. Thus, we must say something about their relation explicitly even with the metaprinciple, if we adopt the conventional second laws that do not mention anything about chemistry.

materially throughout the process; only before and after the process the materials coordinates of the system must be 'the same'[180] (→**4.9**).

This principle, together with the metaprinciple **8.4**, implies that as long as the state is in $\mathcal{E}$, the internal energy may be increased without altering the operational coordinates before and after the process.[181]

Remark 1 Note that this is not a principle solely for closed systems. Furthermore, chemical reactions may occur freely. The conventional thermodynamic textbooks never mention materials changes/chemical reactions. When the second law is introduced, at least a clear statement about the 'equivalence' of work and mass action in contradistinction to heat must be made.

Remark 2: 'Halting chemical reactions at will' cannot save chemical thermodynamics The standard approach, when stated honestly, explicitly assumes that we can halt chemical reactions at any time without disrupting the system equilibrium (→**4.16**). With this assumption + the conventional Planck's principle mentioned at the beginning of this unit, can we develop chemical thermodynamics? Since reactions can be halted at any time, we can treat chemical composition variables and internal energy as independent variables. Thus, even with chemical reactions present in the system, the conventional Planck's principle can be made meaningful. However, the principle makes sense only while the reactions are suspended. To discuss the true chemical equilibria of the system we must release the chemistry from our artificial grip and allow the chemical reactions to proceed. Unfortunately, at that point, the conventional Planck's principle loses its meaningfulness, since nothing is stated about chemical reactions. Thus, we are forced to develop chemical thermodynamics without the second law.

8.6 Clausius' principle implies Planck's principle

If Planck's principle does not hold, we can decrease the system internal energy adiabatically without changing the operational coordinates. Since we cannot export energy as heat adiabatically, the system must have performed some (generalized) work on its environment. That is, we can extract work without modifying the operational coordinates.[182]

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[180] The choice of materials coordinates for a given state is not unique, so what is meant by 'the same' is that we can choose the identical materials coordinates before and after the process.

[181] This corresponds to S1: the existence of irreversible process of Lieb and Yngvason.

[182] Remark: if we choose chemical composition coordinates $\tilde{\boldsymbol{N}}$ instead of $\boldsymbol{N}$ (→**4.16**) as basic thermodynamic coordinates just as in the conventional textbooks, no change of energy while fixing

Prepare a cooler heat bath (→**8.8**) and a hotter heat bath (Fig. 8.1).
(i) Bring the system and the cooler heat bath into thermal equilibrium through thermal contact (→**7.12**).
(ii) Then, thermally isolate the system from the heat bath and obtain work adiabatically from the system without changing its operational coordinates (violating Planck's principle).[183]
(iii) Next, bring the system into thermal contact with the cooler heat bath; note that the procedure can bring the system completely to the original state as prepared in (i). If heat flows out from the system or there is no heat exchange at all, the first law (the conservation of energy) is violated, so to return to the original state given in (i) the heat must be brought to the system from the heat bath. Thus, the cooler heat bath must have lost energy as heat, which was already converted to generalized work. Therefore,
(iv) We can then add this work as heat to any hot heat source according to Mayer-Joule's principle (→**7.14**), violating Clausius' principle.

Therefore,[184] if Clausius' principle holds, Planck's principle must hold as well.

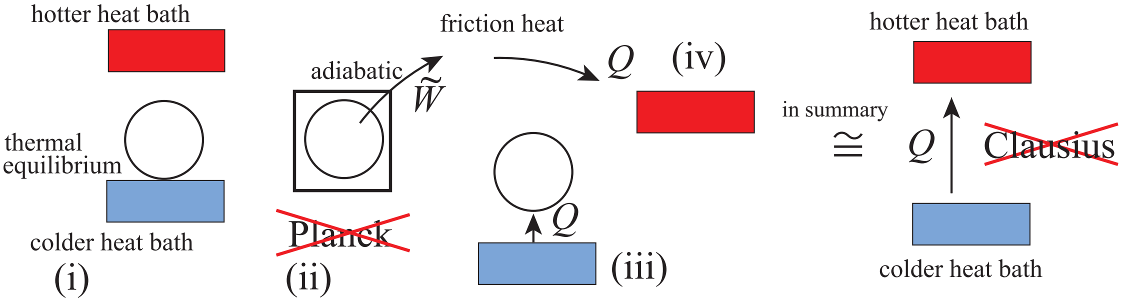

Figure 8.1: Clausius' principle implies Planck's principle

Fig. 8.1 Clausius' principle implies Planck's principle.

(i) Bring the system and the cooler heat bath in thermal equilibrium through thermal contact.

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the chemical composition is generally possible; that is, Planck's principle loses its meaning. This difficulty cannot be removed even if chemical reactions may be halted at any time as assumed in the standard textbooks (→Remark 2 in **8.4**).

[183] Notice that this may not be a cycle for the chemical composition; the system may have done electrochemical work.

[184] Recall $(\neg B \Rightarrow \neg A) \iff (A \Rightarrow B)$. For example, "If not mortal, it is not alive." This means "if alive, it is mortal." This is the relation between a proposition and its contraposition. This relation is always used in the demonstration of the equivalence of the principles in thermodynamics (→**8.9**, **8.10**, **8.13**).

(ii) Then, thermally isolate the system and obtain (generalized) work $\tilde{W}$ from the system without changing its operational coordinates (violating Planck's principle).
(iii) Next, bring the system in thermal contact with the cooler heat bath again; Heat Q flows to the system, whose state returns to that in (i), but the heat Q was converted to $\tilde{W}$ in (ii). [Incidentally, Thomson's principle (→**8.7**) is also violated, so Thomson's principle is shown to imply Planck's principle.]
(iv) We can add $\tilde{W}$ as heat to any hot heat source according to Mayer-Joule's principle (→**7.14**), violating Clausius' principle.

8.7 Thomson's principle

Thomson's principle may be stated as[185]

> It is impossible to do generalized work without leaving any trace other than absorbing heat from a single heat bath.

Here, the condition "without leaving any trace" is quite important (Fig. 8.2);

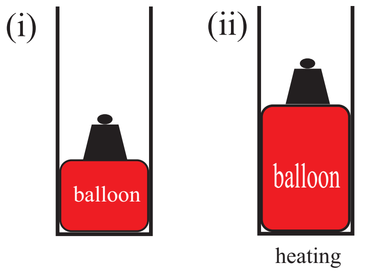

Figure 8.2: Doing work with a single heat source 'with a trace'

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[185] The conventional Thomson's principle is stated without taking any chemical reactions into account, but we must explicitly state 'generalized work' in the principle to construct chemical thermodynamics properly.

Tasaki requires the following form of 'Kelvin's principle' and then applies it to chemical reactions: For any isothermal cycle at temperature T, the work done by the system cannot be positive: that is, $W \leq 0$ must hold.

While his system is based on isothermal systems, the formulation is different from ours. Still with the conventional specification of the amounts of chemicals, we encounter the following problem: if $W \neq$, it is very likely that after 'the cycle' for work coordinates, the system equilibrium states will be different. Consequently, if chemical reactions exist, their equilibria generally shift. This implies that if we demand a true isothermal cycle to be realized, then, generally speaking, only $W = 0$ is allowed. Thus, to formulate Kelvin's principle with chemical reactions we must demand, as Tasaki later does with chemistry, that the reactions may be freely regulated by the experimenter. In particular, all the reactions are halted to make sense of Kelvin's principle. This means that we cannot apply the second law to chemical reactions.

for example, if we warm a balloon, we can do some work with a single heat bath, but after doing the work, the balloon stays inflated, so the production of work with a single heat bath in this case does not violate Thomson's principle.

Clausius regarded a 'work source' (a device to produce work) as the heat bath hotter than any ordinary heat baths (→**A.12**), so it cannot absorb heat from any heat bath. In this sense, Clausius' principle implies Thomson's principle.

The metaprinciple (→**8.4**) implies: "If there are several heat baths not mutually in thermal equilibrium, we can make a device producing (generalized) work without leaving any trace other than exchanging heat with these heat baths."

8.8 Heat source or heat bath

We have already used heat sources or heat baths. A heat bath is a constant temperature environment in thermal contact with a system. While in modern times, it can be realized as a heat pad with high-speed feedback regulation, it is essentially an idealized version of a constant temperature bath. We may imagine a sufficiently large well-stirred water tank, maintained at a constant temperature. However, a heat bath is assumed to be in an equilibrium state at a constant temperature despite interacting with a system. Hence, it cannot be of finite size. Therefore, math-inclined people argue that using such an unrealistic device in the foundational theory of physics is inappropriate.

Consequently, to be precise, theoreticians introduce an increasing sequence of baths and its limit is understood as the idealized heat bath. In practice, a sufficiently large well-stirred bath realizes the idealized heat bath quite accurately.[186]

An ingenious strategy is to use the first order phase transition (→**23.4**), exemplified by Laplace's ice calorimeter (Fig. 8.3). It is a good example, and also historically the first one. Some people criticize this idea as a cheat, since it relies on very special materials properties of particular substances. However, the materialistic diversity of our world is real. Since phase transition temperatures can be continuously fine-tuned, we should note that any heat bath can be devised with Laplace's idea, in

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[186] Mathematical limits in thermodynamics should be taken with a grain of salt. As discussed in **6.5**, thermodynamic infinitesimal is not really mathematical infinitesimal. Consequently, 'infinite' in thermodynamics should be understood as the reciprocal of 'thermodynamic infinitesimal.' That is, it is very big but finite. Thus the 'temperature fluctuation' of a heat bath is invisible from our scale.

In other words, mathematics (analysis) of thermodynamics is mathematics with errors, but those errors cannot be systematically collected to build something we cannot ignore at our scale.

principle.

From the system's perspective, the heat bath assisted by first-order phase transitions cannot be distinguished from suitable heat pads when high-speed feedback control is employed.

In any case, since the idea of heat bath is quite natural, heat baths will be used freely without any hesitation throughout these lecture notes.

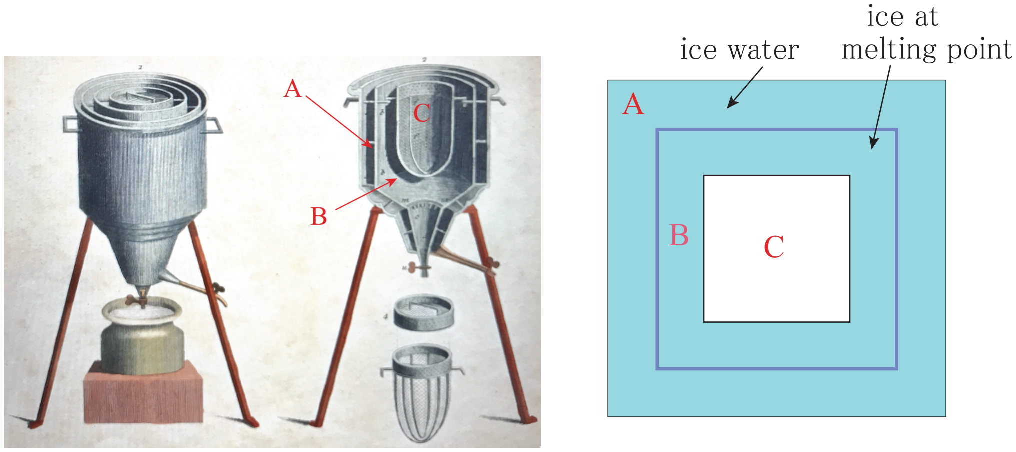

Figure 8.3: Laplace's ice calorimeter

Fig. 8.3 Laplace's ice calorimeter

Left: According to Wikipedia Calorimeter (part; however, the original photo has been cleaned). A contains ice-water and B contains 0 °C ice. A contains the ice to realize adiabaticity, so the formed water is discarded through the spout, if necessary. The water due to the melting in B is collected by the container and is weighed.

Right: a schematic figure. Both A and B are maintained at 0 °C due to the melting ice, so no net heat exchange exists between them. That is, B+C is an adiabatic system. The melting of the 0 °C ice in B is used to measure the heat generated in C. A is used as a heat bath kept at 0 °C.

8.9 Planck's principle implies Thomson's principle

If Thomson's principle (→**8.7**) does not hold, we can prepare a single heat bath engine. This engine may be joined with a heat storage device that does not change its operational coordinates while absorbing or releasing heat.[187] After supplying heat

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[187] Precisely speaking, as noted in **C.3** explicitly, we must assume that we can, in principle, change the system internal energy without changing its operational coordinates. This assumption is not an artificial one and has already been used to state Planck's principle (→**8.5**).

to the heat storage, we can enclose the engine and the heat storage with adiabatic walls and consider the whole as a single adiabatic system. Operating the system we can produce work adiabatically without changing the operational coordinates of the system (→Fig. 8.4). Therefore, Planck's principle is violated. Thus, if Planck's principle holds, then Thomson's principle must also hold.

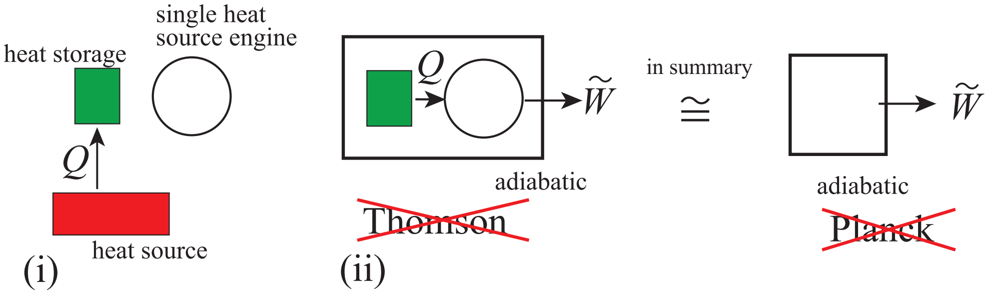

Figure 8.4: Planck's principle implies Thomson's principle

Fig. 8.4 Planck's principle implies Thomson's principle.

(i) Maintaining the operational coordinates of the heat storage, heat Q is introduced to it from the external heat source.

(ii) The total system is thermally isolated, and then the single-heat source engine is operated to convert heat Q to generalized work $\tilde{W}$.

As a single system, this process violates Planck's principle.

8.10 Thomson's principle implies Clausius's principle

Thomson's principle (+ metaprinciple **8.4**) allows us to prepare a heat engine that produces work W while absorbing heat Q from a hotter heat source and discarding heat Q' to a cooler heat source **8.7**).[188] If we assume that Clausius's principle can be violated, then heat Q' may be transferred to the hotter heat bath without leaving any trace other than this heat transfer (Fig. 8.5). Thus, we have realized a single heat source engine,[189] so Thomson's principle is violated. Thus, if Thomson's principle holds, so does Clausius' principle.

Fig. 8.5 Thomson's principle implies Clausius' principle.

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[188] This does not mean that any choice of W, Q, Q' such that $W = Q - Q'$ is possible as Carnot's theorem (→**A.8**) implies.

[189] We could even transfer heat from the cooler to the hotter heat bath, while producing work.

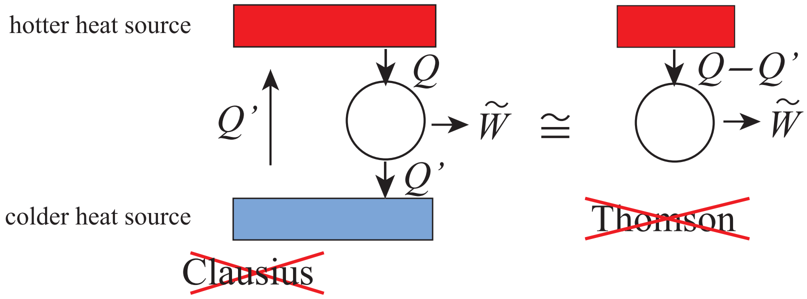

Figure 8.5: Thomson's principle implies Clausius' principle

If we deny Clausius' principle, the exhaust Q' of engine may be returned to the hotter heat source, and we can realize the single heat source engine, violating Thomson's principle.

8.11 Three principles are equivalent

So far, we have demonstrated Clausius ⇒ Planck ⇒ Thomson ⇒ Clausius (→**8.6**, **8.9**, **8.10**). Therefore, all the principles are equivalent.

8.12 Isn't there any revision of Clausius' principle due to chemical reactions?

As already stated in **8.5** (especially Remark 2) and **8.7**, both Planck's and Thomson's principles, as presented in conventional textbooks, require revision in the world where chemistry is relevant. How about Clausius' principle?

Clausius' principle holds true in any world with or without chemistry, and thus does not require revision. However, the principle is equivalent to other principles in a particular world, so even if we can demonstrate the equivalence of Clausius' principle with, say, Planck's principle in a world without chemistry (that is the usual version of this principle), this demonstration is meaningful only in such a world.[190]

8.13 Carnot's principle

In the paper that established thermodynamics, Clausius demonstrated that if there were a heat engine that was more efficient than a reversible engine, (the so-called) Clausius' principle would be violated (→**A.10**) as explained in Fig. **??**. Since the second law of thermodynamics follows from Carnot's theorem that there is no engine more efficient than a reversible engine (see just below), We may call "There is no more efficient engine than a reversible engine," or more simply, "The efficiency of a heat engine has an upper bound less than 1" as Carnot's

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[190] A metaphor: in an additive group G the unit element '0' must satisfy $0 + x = x$ for any $x \in G$, so for a finite field, $\mathbb{R}$ or $\mathbb{Z}$ the same law must hold, but the proof that something is equal to 0 in a finite field may not necessarily apply to $\mathbb{R}$.

principle.

To derive Clausius' principle from Carnot's principle is trivial now. If we deny Clausius' principle, Thomson's principle is violated, so we can make a heat engine whose efficiency is 1, thus violating Carnot's principle. Therefore, all the principles so far stated are equivalent: Carnot $\equiv$ Clausius $\equiv$ Thomson $\equiv$ Planck.

9 Partial derivatives and differential forms

From now on, we need rudiments of analysis of multivariable functions. Thus, necessary mathematical topics are collected here for convenience. This is not a comprehensive introduction to the subject, so the reader is expected to have studied serious introductory textbooks on analysis. The reader may skip this section, and return to it later, if needed.[191]

9.1 Partial derivative and directional derivative

The reader is expected to be familiar with the rudiments of multivariable analysis, e.g., continuity of multivariable functions. Partial differentiation is assumed to be well understood; for example, the partial differentiability of a two variable function $y = f(x_1, x_2)$ with respect to x_1 is the differentiability of f with fixed x_2 as a single variable function of x_1.[192]

Along a line we may interpret f as a single variable function. If it is differentiable, the derivative along the line is called the *directional derivative*. The directional derivative along a specific coordinate direction is the usual partial derivative.

One challenge with multivariable functions is that partial differentiability of a function at a point does not even guarantee its continuity there. Even if all the directional derivatives at the origin is well defined, the function may not be continuous at the origin. See

$$f(x,y) = \left\{ \begin{array}{cl} x^2y/(x^4+y^2) & \text{if } (x,y) \neq (0,0) \\ 0 & \text{if } (x,y) = (0,0) \end{array} \right. . \tag{9.1}$$

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[191] Lieb and Yngvason [The physics and mathematics of the second law of thermodynamics, Phys. Rep. **310**, 1 (1999)] write on p10: “Giles’ work and ours use very little of the calculus. Contrary to almost all treatments, and contrary to the assertion (Truesdell and Bharata, 1977) that the differential calculus is the appropriate tool for thermodynamics, we and he agree that entropy and its essential properties can best be described by maximum principles instead of equations among derivatives. To be sure, real analysis does eventually come into the discussion, but only at an advanced stage (Section 3 and Section 5 in our treatment).”

The author agrees with them, if we do not worry about how work and energy are obtained in the macroscopic physics or how macroscopic physics is practiced. However, it is important to recognize that thermodynamics is not a standalone discipline separate from physics and chemistry (→**1.8**). Therefore, it is natural to express work in terms of the work form (→**3.10**). Consequently, analysis becomes an integral part of this exposition.

[192] Needless to say, for this to be possible, x_1 and x_2 must really be independent. It is a trivial statement, but, as we will see later, we must take it very seriously as alluded in **9.8**.

In this case, along any line going through the origin f goes to zero continuously, but along $(x, y) = (t, t^2)$ with $t \to 0$ f goes to $1/2$ at the origin.[193]

9.2 Notation for partial derivatives in thermodynamics

In mathematics, the partial derivative of $f(x, y)$ with respect to x and y are written, respectively, as

$$\frac{\partial f}{\partial x} \text{ and } \frac{\partial f}{\partial y}. \tag{9.2}$$

In this notation the former is understood that y is kept constant, and the latter x.

In the tradition of thermodynamics, however, the independent variables kept constant are explicitly designated as

$$\left(\frac{\partial f}{\partial x}\right)_y, \left(\frac{\partial f}{\partial y}\right)_x. \tag{9.3}$$

The reason is that in thermodynamics, when f is differentiated with respect to x, what is fixed may not be y, but something else, say, $z = x - y$. In mathematics, in such a case f is regarded as another function g of x and z such that $f(x, y) = g(x, z)$ and the partial derivative must be written as

$$\left(\frac{\partial f}{\partial x}\right)_z = \frac{\partial g}{\partial x}. \tag{9.4}$$

Example: Let $f(x, y) = (x^2 - y^2)\tan y$ and $z = x - y$. Compute the following partial derivatives in the thermodynamic notation and express them in terms of x and y.

$$\left(\frac{\partial f}{\partial x}\right)_y, \left(\frac{\partial f}{\partial x}\right)_z, \left(\frac{\partial f}{\partial z}\right)_x. \tag{9.5}$$

Answer:

$$\left(\frac{\partial f}{\partial x}\right)_y = \frac{\partial f}{\partial x} = 2x\tan y \tag{9.6}$$

is clear. To differentiate f with respect to x while keeping z constant means that $f(x, y)$ is rewritten as a function of x and z as $g(x, z)$:

$$g(x, z) = f(x, x - z) = z(2x - z)\tan(x - z) \tag{9.7}$$

---

[193] taken from R. E. Gelbaum and J. M. H. Olmsted, *Counterexamples in Analysis* (Holden-Day, Inc., San Francisco, 1964). This is a very useful book.

and then partial differentiate it with respect to x. Therefore,

$$\left(\frac{\partial f}{\partial x}\right)_z = \frac{\partial g}{\partial x} = 2z\tan(x-z)+z(2x-z)/\cos^2(x-z) = 2(x-y)\tan y+(x^2-y^2)/\cos^2 y, \tag{9.8}$$

$$\left(\frac{\partial f}{\partial z}\right)_x = \frac{\partial g}{\partial z} = 2(x-z)\tan(x-z)-z(2x-z)/\cos^2(x-z) = 2y\tan y-(x^2-y^2)/\cos^2 y. \tag{9.9}$$

In passing, why don't you confirm Young's theorem **9.7** below? Indeed, we have

$$g_{xz} = g_{zx} = 2\tan y - 2(x-2y)\sec^2 y - 2(x^2-y^2)\tan y\sec^2 y. \tag{9.10}$$

Why does not thermodynamics adopt an explicit function designation as in standard mathematics?

In mathematics f is a symbol for a function, and a function is defined including its independent variables (and the domain), but in thermodynamics the symbol f denotes a particular physical quantity such as internal energy E or pressure P and not simply a function. Therefore, its independent variables depend on various situations. For the above example f and g are distinct as functions, but if they denote the same physical quantity, they are denoted by the identical symbol f in thermodynamics. This can make it unclear what the independent variables are when partial derivatives are computed. That is why the notation as (9.3) is essential in thermodynamics.

9.3 (Strong) differentiability

For a multivariable function to have a tangent plane at a point, it is quite insufficient that the function is partial differentiable at the point (recall the example in **9.1**). If a multivariable function has a tangent plane at a point, it must be *(strongly) differentiable* there:[194] Let $\Delta f = f(x_1+\Delta x_1, x_2+\Delta x_2) - f(x_1, x_2)$. If we can choose constants A and B such that

$$\Delta f = A\Delta x_1 + B\Delta x_2 + o\left[\sqrt{\Delta x_1^2 + \Delta x_2^2}\right] \tag{9.11}$$

holds,[195] then we say f is differentiable at (x_1, x_2). That is, differentiability means

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[194] Often this differentiability is called *strong differentiability* (especially in functional analysis), but, henceforth, we will not always use this terminology, except when we emphasize that strong differentiability is distinct from the mere existence of all the partial derivatives.

[195] o: A quantity $q(x)$ dependent on x satisfies $q(x) = o[x]$ near $x = 0$, if $\lim_{x\to 0} q(x)/x = 0$. In other words, $q(x) = o[x]$ means that q is a higher order infinitesimal than x. For example, $x^{1.01} = o[x]$.

that we can use a linear approximation of the function locally.

If f is differentiable, A and B are given by partial derivatives, so we write

$$df = \frac{\partial f}{\partial x_1}dx_1 + \frac{\partial f}{\partial x_2}dx_2, \tag{9.12}$$

and call df the *total derivative* of f. Do not forget that for this to hold, partial differentiability is not enough, but we need strong differentiability of f.

9.4 Condition for (strong) differentiability

Theorem If all the partial derivatives of a function exist at a point and are all continuous there, then the function is strongly differentiable there.

Let us demonstrate this for a two variable function. If we apply the mean value theorem for x_1 and x_2, respectively, to

$$\begin{aligned} \Delta f &= f(x_1+\Delta x_1, x_2+\Delta x_2) - f(x_1, x_2) && (9.13)\\ &= [f(x_1+\Delta x_1, x_2+\Delta x_2) - f(x_1, x_2+\Delta x_2)] + [f(x_1, x_2+\Delta x_2) - f(x_1, x_2)], && (9.14) \end{aligned}$$

we can write with $\theta, \theta' \in (0,1)$

$$\Delta f = f_{x_1}(x_1+\theta\Delta x_1, x_2+\Delta x_2)\Delta x_1 + f_{x_2}(x_1, x_2+\theta'\Delta x_2)\Delta x_2 + o\left[\sqrt{\Delta x_1^2+\Delta x_2^2}\right]. \tag{9.15}$$

Here, the standard abbreviations for partial derivatives are used:

$$\frac{\partial f}{\partial x} = f_x, \quad \frac{\partial^2 f}{\partial x \partial y} = f_{yx} \quad \text{[note the order of independent variables], etc.} \tag{9.16}$$

Since we have assumed that the partial derivatives are continuous, when Δx_1 and Δx_2 tend to zero, we see (9.15) converges to (9.12). It should be clear that even if the number of variables is more than 2, the same logic applies.

9.5 The expression of total derivative in terms of gradient

For an n-variable function f that is partial differentiable

$$\text{grad} f = \left(\frac{\partial f}{\partial x_1}, \cdots, \frac{\partial f}{\partial x_n}\right) \tag{9.17}$$

is called the *gradient* (or the *gradient vector*) at $x = (x_1, \cdots, x_n)$. In terms of the gradient vector, the total derivative (9.12) reads (if f is strongly differentiable →**9.3**)

$$df = \mathrm{grad} f \cdot dx. \tag{9.18}$$

The multivariable Taylor expansion of f around x_0 to the first order may be written as

$$f(x) = f(x_0) + \mathrm{grad} f(x_0) \cdot (x - x_0) + o[\|x - x_0\|]. \tag{9.19}$$

9.6 Exchanging the order of partial differentiations

Since the partial derivative $\partial f/\partial x_1$ is a function of x_1 and x_2, we may conceive their partial derivatives (second order partial derivatives). The same applies to $\partial f/\partial x_2$ as well. Then, we can make two 'mixed' second-order partial derivatives, partial differentiation with x_1 first or that with x_2 first.

Theorem If $f_{x_1x_2}$ and $f_{x_2x_1}$ are both continuous in a domain, then $f_{x_1x_2} = f_{x_2x_1}$ in the domain.

We can show this as follows. In a neighborhood of a point (a, b) in the domain, let

$$\Delta = f(a + \Delta x_1, b + \Delta x_2) - f(a + \Delta x_1, b) - f(a, b + \Delta x_2) + f(a, b). \tag{9.20}$$

Applying the mean value theorem with respect to x_1 to $f(x_1, b + \Delta x_2) - f(x_1, b)$, we can choose $\theta \in (0, 1)$ such that

$$\Delta = \Delta x_1 [f_{x_1}(a + \theta \Delta x_1, b + \Delta x_2) - f_{x_1}(a + \theta \Delta x_1, b)]. \tag{9.21}$$

Applying the mean value theorem with respect to x_2, we can choose $\theta' \in (0, 1)$ such that

$$\Delta = \Delta x_1 \Delta x_2 f_{x_1x_2}(a + \theta \Delta x_1, b + \theta' \Delta x_2). \tag{9.22}$$

Using the assumption about the continuity of the second order partial derivatives, we have

$$\lim_{(\Delta x_1, \Delta x_2) \to (0,0)} \Delta/\Delta x_1 \Delta x_2 = f_{x_1x_2}(a, b). \tag{9.23}$$

If we repeat the same computation starting with x_2 instead of x_1, we get

$$\lim_{(\Delta x_1, \Delta x_2) \to (0,0)} \Delta/\Delta x_1 \Delta x_2 = f_{x_2x_1}(a, b). \tag{9.24}$$

9.7 Young's theorem[196]

However, in thermodynamics, we may not assume the continuity of second-order partial derivatives, so the theorem in **9.6** is of limited use. It is much more convenient that we can claim the exchangeability of partial differentiations from the mere existence of all the second-order partial derivatives.

Theorem [Young] If f_{x_1} and f_{x_2} are both partial differentiable at a point, $f_{x_1x_2} = f_{x_2x_1}$ there.

We can show this as follows. In (9.21) set $\Delta x_1 = \Delta x_2$ and introduce

$$f_{x_1}(a+\theta\Delta x_1, b+\Delta x_1) = f_{x_1}(a,b)+\theta\Delta x_1 f_{x_1x_1}(a,b)+\Delta x_1 f_{x_1x_2}(a,b)+o[\Delta x_1] \tag{9.25}$$

and

$$f_{x_1}(a+\theta\Delta x_1, b) = f_{x_1}(a,b)+\theta\Delta x_1 f_{x_1x_1}(a,b)+o[\Delta x_1]. \tag{9.26}$$

We obtain

$$\Delta = \Delta x_1^2 f_{x_1x_2}(a,b)+o[\Delta x_1^2]. \tag{9.27}$$

Thus,

$$\lim_{\Delta x_1\to 0} \Delta/\Delta x_1^2 = f_{x_1x_2}(a,b). \tag{9.28}$$

Even if we exchange x_1 and x_2, the assumption in the theorem does not change, so we get $f_{x_1x_2} = f_{x_2x_1}$.

9.8 Remark on the domain of the function and its partial derivatives

Note that the partial derivatives of f are not always well defined at the boundary of its domain. For example, if $f(x,y)$ is defined only on a smooth curve C: $(x(\alpha), y(\alpha))$ on the xy-plane parameterized by α,

$$\frac{df}{d\alpha} = f_x\frac{dx}{d\alpha} + f_y\frac{dy}{d\alpha} \tag{9.29}$$

is not meaningful if f is not defined on the tubular neighborhood of C. f may not be defined outside C. Therefore, neither f_x or f_y may be defined.

The above is a trivial remark: it gives an example of f not differentiable with respect to, say, x if f is confined to C, but we encounter analogous situations in thermodynamics very often. For example, if we wish to express a thermodynamic quantity $S = S(E, V, \tilde{\boldsymbol{N}})$ in terms of the chemical composition $\tilde{\boldsymbol{N}}$, the partial derivative of S with respect to E is impossible, since fixing $\tilde{\boldsymbol{N}}$ usually fixes E as well.[197] If we write the totality of $\boldsymbol{N}$ as $\mathcal{C}$ and that of $\tilde{\boldsymbol{N}}$ as

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[196] due to William Henry Young (1863-1942) `https://en.wikipedia.org/wiki/William_Henry_Young`.

[197] This is a dire mathematical difficulty, if chemical reactions occur. Therefore, conventional textbook require that chemical reactions can be stopped freely at any time to avoid this problem. Certainly, the difficulty mentioned here may be evaded, but as has already been pointed out in **4.16**, we will encounter much more fundamental difficulty.

W, $R_{E,\boldsymbol{X}}$: $\mathcal{C} \mapsto W$ is a retraction, so it is meaningful to introduce the materials coordinates as $S = S(E, V, R_{E,\boldsymbol{X}}(\boldsymbol{N}))$. We realize that the partial derivative of S with respect to E is possible, even if $\boldsymbol{N}$ is fixed.

9.9 Differential forms

Let $f_1, \cdots, f_n$ be functions of n variables. The following linear combination

$$\omega = \sum_{i=1}^{n} f_i dx_i \tag{9.30}$$

is called a *1-form.* (9.18) is an example.

9.10 Exact form

If a 1-form ω is written as the total derivative of a function, that is, if, as (9.18), we can write $\omega = df$, ω is called an *exact form.*

9.11 External differentiation

For differential forms we can define an operation d called *external differentiation*:
(i) If operated on a function f, it gives the total derivative (→**9.3**):[198]

$$df = \sum \frac{\partial f}{\partial x_i} dx_i. \tag{9.31}$$

(ii) d operated on the differential of independent variables vanish: $d(dx_i) = 0$.

For the product of differentials, we use $\wedge$ (wedge), and the following anti-commutativity is assumed:

$$dx_1 \wedge dx_2 = -dx_2 \wedge dx_1. \tag{9.32}$$

Consequently, the product of the same vanishes: $dx_1 \wedge dx_1 = 0$. Otherwise, just as the ordinary multiplication the combination and distributive rules hold.

$dx_1 \wedge dx_2$ may be interpreted intuitively as the area of a rectangle formed by two infinitesimal vectors: dx_1 along the x_1 axis and dx_2 along x_2. If we understand that the area changes its sign when the rectangle is flipped over, we can see that $dx_2 \wedge dx_1$ corresponds to the rectangle being flipped over.[199]

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[198] In mathematics f is often assumed to be infinite times differentiable; in this unit we assume functions are as many times differentiable as needed.

[199] Recall the vector product.

(iii) $d(f dx) = df \wedge dx$.[200]

If we externally differentiate (9.12) using (iii) and assuming f is twice differentiable, Young's theorem **9.7** implies $d^2 f = 0$:

$$\begin{aligned} d^2 f &= df_{x_1} \wedge dx_1 + df_{x_2} \wedge dx_2 && (9.33)\\ &= (f_{x_1x_1}dx_1 + f_{x_1x_2}dx_2) \wedge dx_1 + (f_{x_2x_1}dx_1 + f_{x_2x_2}dx_2) \wedge dx_2 && (9.34)\\ &= f_{x_1x_1}dx_1 \wedge dx_1 + f_{x_1x_2}dx_2 \wedge dx_1 + f_{x_2x_1}dx_1 \wedge dx_2 + f_{x_2x_2}dx_2 \wedge dx_2 && (9.35)\\ &= f_{x_1x_2}dx_2 \wedge dx_1 + f_{x_2x_1}dx_1 \wedge dx_2 && (9.36)\\ &= (f_{x_2x_1} - f_{x_1x_2})dx_1 \wedge dx_2 = 0. && (9.37) \end{aligned}$$

As can be seen from this, we generally have $d^2 = 0$.

9.12 Closed form

If a 1-form

$$\omega = \sum_i f_i(x_1, \cdots, x_n)dx_i \tag{9.38}$$

is externally differentiated to give $d\omega = 0$, ω is called a *closed form*. As can be seen readily by computation, if

$$\frac{\partial f_i}{\partial x_j} = \frac{\partial f_j}{\partial x_i}, \tag{9.39}$$

ω is closed. (9.39) is called *Maxwell's relation* in thermodynamics.

The relation implies the exchangeability of the order of partial differentiation, if $\omega = dF$ (→**9.7**):

$$\frac{\partial^2 F}{\partial x_i \partial x_j} = \frac{\partial^2 F}{\partial x_j \partial x_i}. \tag{9.40}$$

9.13 Poincaré's lemma

As we have seen in **9.12**, an exact form is a closed form. Is the converse true? That is, is there a function F such that $\omega = dF$, if $d\omega = 0$? This holds on a one-point contractible domain (→**5.7**). This is called Poincaré's lemma.[201]

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[200] This is a very special case of the external differentiation of general products.

[201] The totality of equilibrium states $\mathcal{E}$ is a one-point contractible set in the thermodynamic space (→**5.9**), so Maxwell's relation for internal energy is equivalent to the first law of thermodynamics (if E is twice differentiable; this is, however, not always true).

9.14 Line integration

Here, for simplicity, we discuss curves that can be parameterized with a (piecewise) C^1-function.

Let C be a continuous curve with length[202] in n-space.[203] We assume that the curve C is parameterized by a (piecewise) C^1-function $c(t)$. Integrating the 1-form (9.38) with the parameterization $x = c(t)$ implies

$$\int_C \omega = \int_0^1 dt \sum_i f_i(c(t)) \cdot c'(t) dt. \tag{9.42}$$

In the domain where the 1-form is defined, to integrate an exact form $\omega = dF$ along a curve $x = c(t)$ connecting A and B gives, since $c(0) = A$ and $c(1) = B$,

$$\int_C \omega = \int_0^1 \frac{df(c(t))}{dt} dt = f(B) - f(A). \tag{9.43}$$

That is, the result of the integral of an exact form depends only on the initial and the final points of the curve.

9.15 Path dependence of line integrals: examples

Since the differentials of state functions (→**5.4**) are exact, if the initial values are known, then the values at the final state can be computed along any path connecting the initial and the final states. (→**9.14**). In particular, if the integration path is a closed curve, the integral vanishes.

To check the exactness of ω, checking its closedness is incomplete. As can be seen from **9.13**, if its domain is one-point contractible, we have only to check $d\omega = 0$. That is, we have only to confirm Maxwell's relations in the domain. For thermodynamics, the totality of equilibrium states $\mathcal{E}$ is one-point contractible (→**5.7**), so this is enough.

To confirm $d\omega = 0$ we have only to compute the external differentiation (→**9.11**)

Let us perform detailed calculations of line integrals of two variable examples.

$$\omega = y^2 dx + 2x(y+1)dy. \tag{9.44}$$

---

[202] ⟪**Continuous curve with length**⟫ If a curve may be parameterized in terms of a (piecewise) C^1-function, by writing $x = c(t)$, the length L of the curve reads

$$L = \int_0^1 \|c'(t)\| dt, \tag{9.41}$$

where $\| \ \|$ is the vector length.

[203] 'n-space' means n-dimensional space. Generally, a geometric object XXX of dimension n will be denoted as n-XXX.

(i) This is not closed: $d\omega \neq 0$.

To show this checking "Maxwell's relations" is one way, but (although actually exactly the same) to use external differentiation (→**9.11**) may be smarter:

$$d\omega = 2ydy \wedge dx + 2(y+1)dx \wedge dy = [2(y+1) - 2y]dx \wedge dy \neq 0. \tag{9.45}$$

(ii) The line integral of ω depends on the actual path: to integrate ω from the origin to $(1,1)$, let us compare the path A: along $y = x^2$, and B: along $x^2 + (y-1)^2 = 1$.

To perform a line integral parameterizing the path is convenient.
A: $x = t$, $y = t^2$ ($t \in [0,1]$)

$$\int_{y=x^2 \text{ for } x=0\to 1} [y^2dx + 2x(y+1)dy] = \int_0^1 dt\,[t^4dt + 2t(t^2+1)2tdt] \tag{9.46}$$

$$= \int_0^1 dt\,(5t^4 + 4t^2) = 1 + 4/3 = 7/3 \approx 2.33. \tag{9.47}$$

B: Let us write $x = \sin t$, $y = 1 - \cos t$ ($t \in [0, \pi/2]$). Then,

$$\int_0^{\pi/2} [(1-\cos t)^2 \cos t dt + 2\sin t(2-\cos t)\sin t dt] \tag{9.48}$$

$$= \int_0^{\pi/2} dt\,[4 - \cos t - 6\cos^2 t + 3\cos^3 t] \tag{9.49}$$

$$= 2\pi - 1 - 6 \times \frac{\pi}{4} + 3 \times \frac{2}{3} = \frac{\pi}{2} + 1 \approx 2.57. \tag{9.50}$$

Certainly, the integral values depend on the paths.

(2) The following 1-form is exact:

$$\omega = y^2dx + 2xydy. \tag{9.51}$$

(i) Let us confirm $d\omega = 0$.

$$d\omega = 2ydy \wedge dx + 2ydx \wedge dy = [2y - 2y]dx \wedge dy = 0. \tag{9.52}$$

However, this is not generally enough to demonstrate the exactness of ω. For example, let us consider the following 1-form

$$\xi = (-ydx + xdy)/(x^2 + y^2) \tag{9.53}$$

on the unit disk centered at the origin excluding the origin (its domain is not one-point contractible). $d\xi = 0$ and formally we may compute $\xi = d\,\mathrm{Arctan}(y/x)$, but this is not a derivative of a single-valued function.

(ii) Along the same paths A and B above, let us integrate ω. For A

$$\int_{y=x^2 \text{ for } x=0\to 1} [y^2dx + 2xydy] = \int_0^1 dt\,[t^4dt + 2t(t^2)2tdt] \tag{9.54}$$

$$= \int_0^1 dt\,5t^4 = 1. \tag{9.55}$$

For B

$$\int_0^{\pi/2} [(1-\cos t)^2 \cos t dt + 2\sin t(1-\cos t)\sin t dt] \tag{9.56}$$

$$= \int_0^{\pi/2} dt\,[2 - \cos t - 4\cos^2 t + 3\cos^3 t] \tag{9.57}$$

$$= \pi - 1 - 4 \times \frac{\pi}{4} + 3 \times \frac{2}{3} = 1. \tag{9.58}$$

(iii) Since $\omega = d(xy^2)$, of course, $xy^2(x=y=1) - xy^2(x=y=0) = 1$.

9.16 Integral of 2-forms

A linear combination of the wedge products of differentials of two independent variables such as $dx_i \wedge dx_j$ is called a 2-form. In 2-space it is of the following form: $\omega = f dx \wedge dy$. Its integration on a 2-area m is defined as follows:

$$\int_m \omega = \int_m f dx dy. \tag{9.59}$$

The integrals of differential forms are linear with respect to the integrands:

$$\int_m (\omega + \omega') = \int_m \omega + \int_m \omega'. \tag{9.60}$$

The integral of $dy \wedge dx$ is negative of that of $dx \wedge dy$. If m is a small rectangle $\varepsilon_x \times \varepsilon_y$ around (x, y), and if f is continuous

$$\int_m \omega \simeq f(x,y)\varepsilon_x\varepsilon_y. \tag{9.61}$$

9.17 Change of independent variables in integrals: Jacobian

Suppose f is a function of (X, Y) and the map: $(X, Y) \mapsto (x, y)$ maps M to m. Then,

$$\begin{aligned}\int_M f(X,Y)dX \wedge dY &= \int_m f(X(x,y),Y(x,y))(X_x dx + X_y dy) \wedge (Y_x dx + Y_y dy) \\ &= \int_m f(X(x,y),Y(x,y))(X_x Y_y dx \wedge dy + X_y Y_x dy \wedge dx) \\ &= \int_m f(X(x,y),Y(x,y))\,[X_x Y_y - X_y Y_x]\,dx \wedge dy. \end{aligned} \tag{9.62}$$

This is a well-known formula for changing independent variables of integrals. The quantity in [ ] is the *Jacobian*:

$$X_xY_y - X_yY_x = \begin{vmatrix} \frac{\partial X}{\partial x} & \frac{\partial Y}{\partial x} \\ \frac{\partial X}{\partial y} & \frac{\partial Y}{\partial y} \end{vmatrix} = \frac{\partial(X,Y)}{\partial(x,y)}. \tag{9.63}$$

That is,

$$dX \wedge dY = \frac{\partial(X,Y)}{\partial(x,y)} dx \wedge dy. \tag{9.64}$$

9.18 Young's theorem or Maxwell's relations in terms of Jacobians

Let $\omega = \sum x_i dX_i$ be an exact 1-form (→**9.10**). Then,

$$0 = d\omega = \sum dx_i \wedge dX_i \tag{9.65}$$

In particular, if only two independent variables are changed, we have

$$0 = dx_i \wedge dX_j + dx_j \wedge dX_i = \left(\frac{\partial x_i}{\partial X_j}\right)_{X_j^c} dX_j \wedge dX_i + \left(\frac{\partial x_j}{\partial X_i}\right)_{X_i^c} dX_i \wedge dX_j. \tag{9.66}$$

This implies Young's theorem (→**9.7**).[204] If we integrate this on the x_iX_i-plane around an infinitesimal square ε around a point, we get (→**9.17**)

$$\int_\varepsilon dx_i \wedge dX_i + \int_\varepsilon dx_j \wedge dX_j = \int_\varepsilon \left[1 + \frac{\partial(x_j, X_j)}{\partial(x_i, X_i)}\right] dx_i dX_i = 0. \tag{9.67}$$

Therefore, if the Jacobian is continuous,[205] Young's theorem or Maxwell's relation is equivalent to

$$\frac{\partial(x_j, X_j)}{\partial(x_i, X_i)} = -1. \tag{9.68}$$

Here, all the variables kept constants are not written for the partial derivatives; as the Jacobian, essentially the 2 × 2 portion need be considered.

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[204] As before, X_i^c in the suffix means that the variable X_i is removed from the total set of independent variables.

[205] Especially, if all the relevant partial derivatives are continuous. Therefore, when we discuss Maxwell's relation, our conclusion holds.

10 Structure of thermodynamic space

10.1 Possibility of reversible and quasistatic adiabatic processes

Let $\mathcal{E}$ be the totality of the equilibrium system of a system under consideration. Take a point $P \in \mathcal{E}$ and let its projection onto the operational coordinate hyperplane be P' (Fig. 10.1).

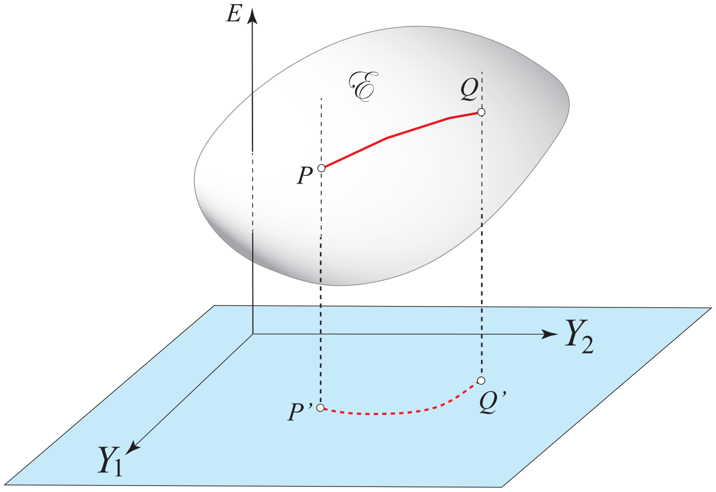

Figure 10.1: The totality $\mathcal{E}$ of the equilibrium states of a system and an adiabatic and reversible-quasistatic process in it; The vertical broken lines denote constant operational coordinate lines. The adiabatic reversible and quasistatic change of operational coordinates from P' to Q' along the red broken curve on the operational coordinate hyperplane (the pale blue plane) results in the change of E according to $dE = \omega + \zeta$ (as illustrated by the red curve P to Q).

Our strategy is to construct thermodynamics based on the non-thermal macroscopic physics and chemistry (→**1.3**). We are allowed to change operational coordinates adiabatically and reversible-quasistatically as long as allowed by non-thermal macrophysics and chemistry. The system internal energy E changes according to the generalized work form (ω in **3.10** + ζ in **4.13**). Consequently, there exists a reversible quasistatic adiabatic process through an arbitrary state $P \in \mathcal{E}$ whose projection onto the $\boldsymbol{Y}$-plane may be specified.[206]

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[206] This says the projection is unique, but for a given projection its 'preimage' need not be unique; for a given curve on the $\boldsymbol{Y}$-plane the curve (corresponding to a reversible-quasistatic and adiabatic process) through P constructed by integrating the generalized work form cannot be demonstrated to be unique by the standard uniqueness argument for the solutions of differential equations, since we

10.2 There is a region not accessible by adiabatic processes from an equilibrium state

The following considerations rely on all the facts, principles, etc., we have so far discussed. In particular, we rely on Planck's principle (→**8.5**) as the second law of thermodynamics (stated here again for convenience):

> **Planck's principle**: By an adiabatic process with the identical initial and the final operational coordinates, the system internal energy cannot be reduced (Fig. 10.2). In paticular, along a line parallel to the energy axis, the system cannot go down adiabatically.

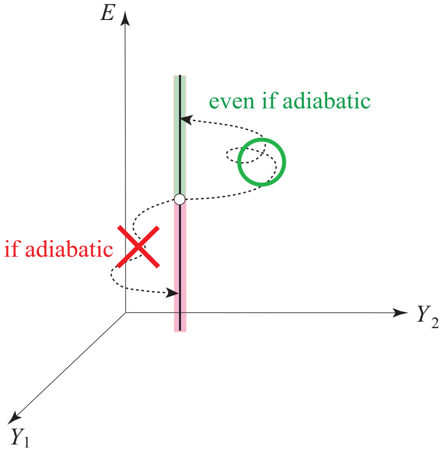

Figure 10.2: Planck's principle: from the state denoted by a small white disk on the vertical line the red-shaded portion cannot be adiabatically reached; the green-shaded portion may be accessible, but not reversibly. The vertical line is a operational-coordinate constant line parallel to the energy axis.

Here, the 'adiabatic process' may be any realizable one whose initial and the final operational coordinates are identical (that is, the initial and the final work and materials coordinates agree).

Remark Planck's principle itself only forbids adiabatic reduction of internal energy. Therefore, it does not say anything about the green states in Fig. 10.2. We take the metaprinciple (→**8.4**) for granted.

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know, at best, only the continuity of the conjugate intensive variables (e.g., we cannot claim Lipshitz continuity). If we use the second law of thermodynamics, we can demonstrate the uniqueness of the process (→**10.3**). For the argument here we only need the existence of a process specified by the projection onto the $\boldsymbol{Y}$-plane; the existence is guaranteed by the first law of thermodynamics.

10.3 Uniqueness of the internal energy change by a reversible and quasistatic adiabatic process

Take a point $P \in \mathcal{E}$ in the thermodynamic space $(E, \boldsymbol{Y})$ (Fig. 10.3). Let the curve P-Q be a result of integrating the generalized work form along P'-Q' on the $\boldsymbol{Y}$-plane as discussed in **10.1**.

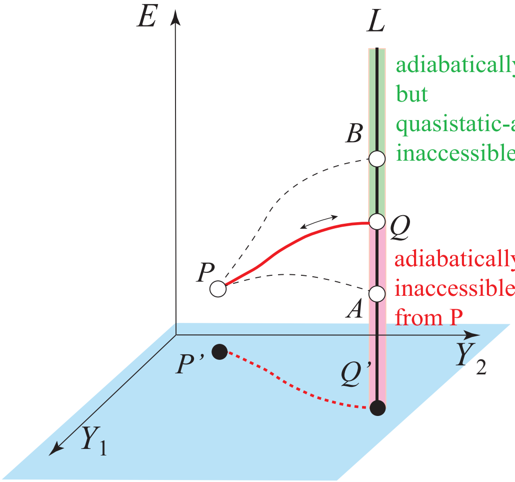

Figure 10.3: Integration of the generalized work form along P'-Q'(the broken red curve on the $\boldsymbol{Y}$-plane as in Fig. 10.1) provides a unique solution curve (red curve). The line L denotes the totality of the states whose operational coordinates are identical to those of Q' (parallel to the energy axis).

Let L be the line going through Q' parallel to the energy axis (Fig. 10.3). In Fig. 10.3 the broken red curve P'-Q' denotes a specified operational coordinate change for a reversible quasistatic adiabatic process (as in Fig. 10.1). Integrating the generalized work form along this curve has not yet been shown to give a unique solution, but the red curve in the figure is understood as a possible integration result as in Fig. 10.1.

Planck's principle tells us that we cannot go to state A that is below Q along L (in the red-shaded portion in Fig. 10.3) from P adiabatically; if possible, since $P \to Q$ is retraceable, we can adiabatically realize $Q \to P \to A$, but Q and A are on L, so this violates Planck's principle.

How about state B in the green-shaded portion above Q in Fig. 10.3? $P \to B$ is not forbidden adiabatically (→**8.4**), but cannot be realized reversibly; if possible $B \to P \to Q$ may be adiabatically realized and Planck's principle is violated.

Thus, we have found that if we integrate the generalized work form along the curve $P' \to Q'$, the integration result is uniquely given by P-Q.

10.4 Construction of reversible adiabatic hypersurface

Take any continuous curve C on the operational coordinate hyperplane spanned by $\boldsymbol{Y}$. We have found in **10.3** that the solution curve $E(C)$ in $\mathcal{E}$ obtained by integrating the generalized work along C starting from P is unique. Since $C \mapsto E(C)$ is a continuous map,[207] there must be a continuous map $\mathcal{A}$ defined on an appropriate convex set on the operational coordinate hyperplane whose range A_P is a hypersurface passing through P such that $\mathcal{A}(C) = E(C)$.

Since A_P is meshed by integration curves of $dE = \sum y_i dY_i$ starting from P,[208] it is strongly differentiable at P and its tangent vector is given by $\boldsymbol{y} = (y_1, \cdots)$.

10.5 Reversible adiabatic hypersurfaces foliate $\boldsymbol{\mathcal{E}}$

Take a hypersurface A_P (curves in it are denoted by the red curves in Fig. 10.4) constructed as in **10.4** and choose an arbitrary point Q on it. Then, construct the adiabatic reversible surface A_Q passing through Q (a curve in it is denoted by the green curve in Fig. 10.4) constructed just following the method in **10.4**. If A_P and A_Q do not agree, then there is a point R in $\mathcal{E}$ such that one of them is above the other along the E axis. Assume at R on A_Q, A_Q is above A_P as illustrated in Fig. 10.4. Then, we are allowed to go along $RQPR'$, where R' on A_P is just below R. Thus, Planck's principle would be violated.

Therefore, A_P and any adiabatic reversible hypersurface sharing a common point must agree:

$$Q \in A_P \Rightarrow A_Q = A_P. \tag{10.1}$$

Therfore, A_P is anywhere strongly differentiable.

10.6 Adiabatic reversible surfaces do not switch their order along the

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[207] Here, the meaning should be clear; to be precise, we must introduce a topology in the set of all continuous curves in the thermodynamic space spanned by E and $\boldsymbol{Y}$. This can be done with the aid of the *Frechét distance* ρ_F: for two continuous curves a and b, $\rho_F(a,b)$ is the shortest length of the leash you need to walk your dog along b while you walk along a, intuitively.

[208] More precisely, we can make an ε-net covering A_P for any positive ε consisting of integration curves of $dE = \sum y_i dY_i$ starting from P. A subset M of A is an *ε-net* of A, if for any $x \in A$ there is $m \in M$ such that distance $\|x - m\| < \varepsilon$.

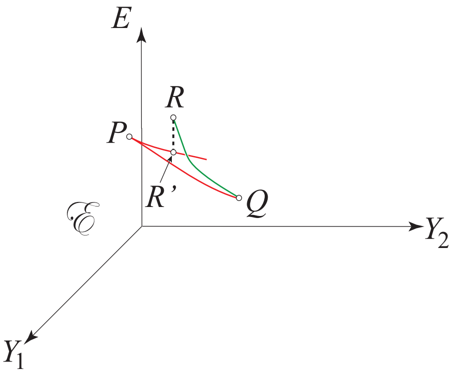

Figure 10.4: The red curve is on A_P and the green on A_Q. The illustration assumes that R on A_Q is above R' on A_P, where R and R' have the same operational coordinates. Along any curve the process is reversible, so $R \to Q \to P \to R'$ is adiabatically realizable, violating Planck's principle.

energy axis

Given an equilibrium state, an adiabatic reversible surface through it is uniquely determined (→**10.4**). Furthermore, $\mathcal{E}$ may be decomposed into mutually exclusive adiabatic reversible surfaces like mille-feuille.[209] The stacking of these hypersurfaces is simple in the following (mathematically standard) sense. Take two adiabatic reversible surfaces. If one is above the other along a line parallel to the E-axis, this ordering is kept along any line parallel to it. Switching ordering as in Fig. 10.5 is not allowed as explained below.

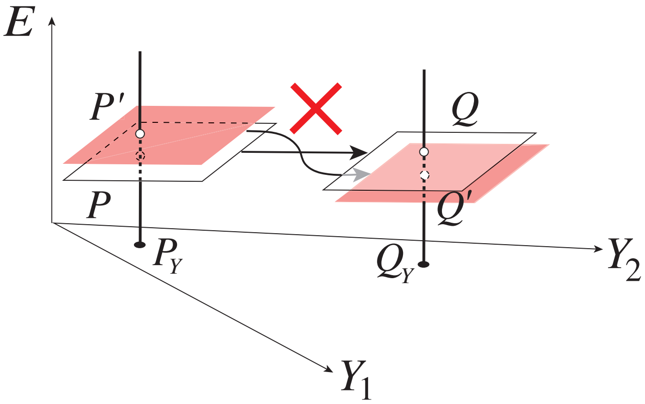

Figure 10.5: The adiabatic reversible surfaces do not switch their ordering along the energy axis. Here, vertical lines are parallel to the energy axis.

Suppose P' and P have the same operational coordinates. We can go from P' to Q' or P to Q adiabatically and reversibly. We can also go adiabatically from Q' to Q

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[209] Mathematically, we cay $\mathcal{E}$ is *foliated* by adiabatic reversible hypersurfaces.

along the line parallel to the energy axis. Then, using the reversibility of P-Q, we can go $P' \to Q' \to Q \to P$ adiabatically. This violates Planck's principle.

10.7 Adiabatic reversible hypersurfaces: summary

Let us summarize the structure of the totality of the equilibrium states $\mathcal{E}$ of a system we have realized so far.

The totality of the equilibrium states of a system $\mathcal{E}$ is separated into hypersurfaces consisting of equilibrium states that may be transformed into (reachable to and from) each other by reversible adiabatic processes (→**10.5**). These hypersurfaces have the same order along any line parallel to the E-axis (→**10.6**).

Any point on a line with constant operational coordinates (i.e., on a line parallel to the E axis) is in one and only one reversible adiabatic hypersurface, so the totality of these hypersurfaces and an interval of the real numbers are one to one continuously correspondent (i.e., homeomorphically correspondent).

Each reversible adiabatic hypersurface A may be constructed by integrating the generalized work form $dE = \sum y_i dY_i$ starting from any single equilibrium state on it. Thus, $(y_1, \cdots, y_m)$ defines a gradient vector field whose potential function is E, and A is strongly differentiable.

Physicochemically speaking, a reversible adiabatic hypersurface A_P describes all the macrophenomena that can happen non-thermally without any dissipation, if the system is initially prepared in state P. In particular, if we forget about chemistry all together, it is the space where all the macroscopic mechanical and electromagnetic phenomena occur, if the system is initially prepared in state P.[210] Therefore, the phenomena that can occur within this hypersurface may be discussed without thermodynamics. Thermodynamics expands the realm of macrophysics/chemistry by making possible to discuss the transitions between these hypersurfaces.

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[210] However, do not forget the constraint that thermodynamics can handle only additive systems (→**2.10**).

C Appendix C. Realizability of paths in the thermodynamic space

C.1 Why we consider the physical realizability of any path

For a given system, the totality $\mathcal{E}$ of its equilibrium states forms a convex set (or a homeomorphic image of a convex set →**5.9**). Therefore, for any two points P and Q in $\mathcal{E}$, there exists a continuous curve that connects them in $\mathcal{E}$. Is this curve realizable as an actual physico-chemical reversible quasistatic process (→**A.6**)?[211]

Thermodynamic textbooks often assume (though not always explicitly) that all processes connecting two equilibrium states in $\mathcal{E}$ are realizable, so the following discussions may be taken for granted (and ignored). However, it is important to explicitly demonstrate the experimental realizability of all continuous paths in $\mathcal{E}$ as reversible and quasistatic processes. Then, we may guarantee the applicability of thermodynamics along any continuous curve in $\mathcal{E}$.

C.2 Adiabatic reversible processes

As discussed in **10.3**, if we integrate the generalized work form $(\omega + \zeta)$ along a continuous curve on $\mathcal{E}_P$ (the hyperplane passing with constant E through P) connecting P and Q' (Fig. 10.2), we obtain a unique solution curve connecting P and a certain point Q (on A_P) with the same operation coordinates as Q'. Therefore, there is an adiabatic reversible and quasistatic process between P and Q.

C.3 Changing E while keeping operational coordinates constant

Planck's principle discusses a state change vertically along a line parallel to the E axis. It states that it is impossible to decrease E along this line adiabatically, while increasing E along the line is adiabatically possible, but the process is practically achieved by heating the system with heat obtained from the dissipation of some work. Therefore, we make the following explicit assumption:[212]

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[211] Do not forget that being quasistatic does not guarantee the retraceability of a process. If there is no interaction with the environment, usually being quasistatic is enough to be retraceable.

[212] If we apply the metaprinciple (→**8.4**), we may claim that non-adiabatic reversible changes may be allowed to move freely along any constant operational coordinate line, but here, to be clear this assumption is stated.

> A system may exchange heat reversibly and quasistatically, as long as its state is in $\mathcal{E}$, with its environment without modifying the operational coordinates.

With this natural assumption, we may claim the existence of a reversible quasistatic process between any two equilibrium states P and Q as shown in **C.4**.

C.4 Any two equilibrium states may be connected by a reversible and quasistatic process

For a given system, the totality $\mathcal{E}$ of its equilibrium states is a convex set (or a homeomorphic image of a convex set →**5.9**). Therefore, any two points P and Q in $\mathcal{E}$ can be connected by a continuous curve in $\mathcal{E}$. Therefore, there must be a reversible and quasistatic process connecting these states.

Can we actually realize a physico-chemical reversible quasistatic process (→**A.6**) connecting any two points P and Q in $\mathcal{E}$?

Choose a state Q' on A_P (→**10.3**) with the same operational coordinates as Q (that is, Q' is the crossing point of the line parallel to the E axis passing through Q and A_P). This construction, as discussed in **10.3**, yields an adiabatic reversible process from P to some state Q' that has identical operational coordinates as Q. If $Q = Q'$, then this adiabatic process is sufficient, but generally these two states are distinct. In that case, we may (→**C.3**) heat or cool the system reversibly while keeping the operational coordinates to bring Q' to Q. Thus, we have shown that there is a reversible quasistatic process between any two equilibrium states.

C.5 Any continuous curve may be realized as a reversible quasistatic process

Since we may assume the thermodynamic space as a Euclidean space (→**5.2**), we can define a distance between two continuous curves connecting the same pair of points.[213] In $\mathcal{E}$ arbitrarily close to a continuous curve connecting P and Q, we can draw a physically realizable continuous process combining adiabatic and reversible continuous curves and line segments parallel to the E axis, so any continuous curve may be physically realized as a reversible quasistatic process.

Therefore, we may connect any pair of states in $\mathcal{E}$ with a reversible quasistatic process that corresponds to any continuous curve in $\mathcal{E}$ connecting the two states.

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[213] There may be many ways, but for example, we can use the Frechét distance.

C.6 There is an adiabatic process between any equilibrium states

Thanks to Mayer-Joule's principle (→**7.14**), we can effectively add heat to the system through supplying work to it. However, Planck's principle (→**8.5**) tells us that we cannot remove heat adiabatically through (generalized) work.

Therefore, if the situation is the Left of Fig. C.1, then there is an adiabatic process from P to Q, because we can irreversibly go from Q' to Q. However, if the situation is the Right of Fig. C.1, then we cannot go from Q' to Q adiabatically. In this case, we can go from Q to Q' adiabatically, so an adiabatic process from Q to P is realizable.[214]

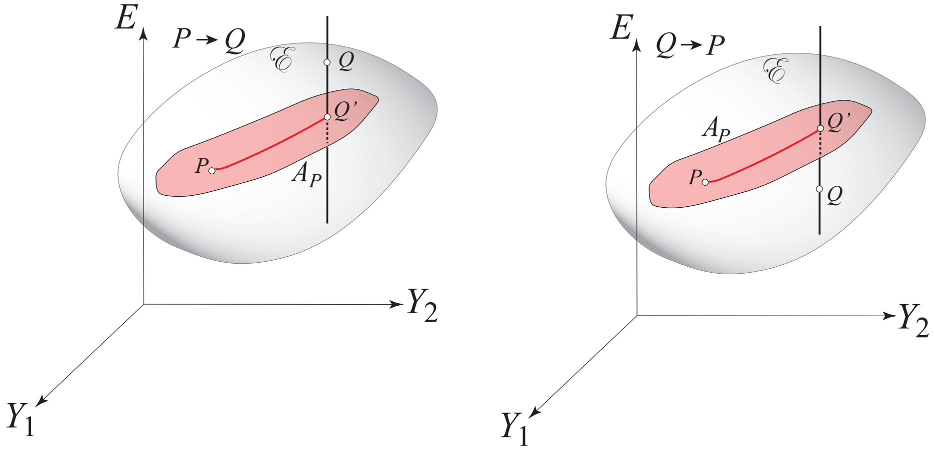

Figure C.1: Left: we can go from P to Q' adiabatically, and if Q' has a smaller internal energy than Q we can go from Q' to Q along the vertical line (irreversibly). Right: if Q is below Q', then we can never go to Q from Q' adiabatically. However, we can adiabatically go from Q to Q'. Since P-Q' is reversible, we can adiabatically go from Q to P.

Thus, we have shown that for any pair of equilibrium states we can adiabatically go from at least one state to the other.

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[214] As noted repeatedly, the chemical compositions of Q and Q' may not be identical.

11 Construction of entropy

11.1 Outline of the logic introducing entropy

As summarized in **10.7** we can foliate $\mathcal{E}$ into smooth leaves (hypersurfaces) that stack continuously along the E axis. We can define a differentiable function S that captures this geometrical structure of $\mathcal{E}$: S is constant on each leaf that corresponds to one adiabatic hypersurface, and can change its value by adding or subtracting heat reversibly (→**C.3**). This function S is called entropy.

11.2 A differentiable state function can be defined that is constant on adiabatic reversible hypersurfaces: an overview

We now know that the totality $\mathcal{E}$ of equilibrium states of a system can be foliated into strongly differentiable adiabatic and reversible hypersurfaces (= *leaves* of the foliation). These leaves are ordered along the E-axis as described in **10.6**. Importantly, each leaf of the foliation can be continuously and one-to-one (i.e., homeomorphically) mapped onto an interval of real numbers.

We may define a function $S = S(E, \boldsymbol{Y})$ that is constant on each leaf. The function is also strictly monotone increasing along the energy axis: for $E < E' \Rightarrow S(E, \boldsymbol{Y}) < S(E', \boldsymbol{Y})$ for each $\boldsymbol{Y}$.

As we will discuss in **11.3**, we may define S as a differentiable function of E under constant $\boldsymbol{Y}$. Combining this fact and the strong differentiability of the leaves of the foliation of $\mathcal{E}$, we can claim that $S(E, \boldsymbol{Y})$ depends on E and $\boldsymbol{Y}$ differentiably (→**11.4**). To demonstrate the strong continuous differentiability of $S(E, \boldsymbol{Y})$, we need a convexity of this function that will be discussed in **13.7**.

Remark. We are to define a state function S to be called 'entropy' that is maximally convenient for thermodynamics. We are not proving that such a quantity exists, but rather trying to construct a convenient state function S that well-captures the natural foliated structure of $\mathcal{E}$.[215]

11.3 Transition between adiabatic hypersurfaces through heat exchange

How can we change the value of the function S?

By definition, if we can change the internal energy of the system without any

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[215] Our attitude is: the foliated structure of $\mathcal{E}$ is fundamental.

change in the operational coordinates (i.e., along a line parallel to the energy axis), we can surely change the value of S. This implies that we can surely change the value of S by adding or subtracting heat. Here, the procedure is performed in the thermodynamic space, so 'exchanging heat' implies 'exchanging heat reversibly and quasistatically'[216] between the system and its environment.

Since S may be defined as a strictly increasing continuous function of E, adding infinitesimal heat $\delta Q > 0$ to the system must increase S (→**11.2**). The change of internal energy is $\delta E = \delta Q$. Therefore, we may demand $\delta S \propto \delta Q$. Thus, we may assume the relation between E and S at least partially differentiable under constant $\boldsymbol{Y}$. Since Q is extensive (→**3.1**), we may assume S to be extensive as well. Thus, we may assume that S is an extensive (not only partition additive →**2.13**) state function that is at least partially differentiable with respect to E.

We wish to emphasize again that we are not proving the existence of a function S that is partially differentiable with respect to E. We are free to construct S in a way that captures the smoothly foliated structure of $\mathcal{E}$ as nicely as possible.

11.4 $\boldsymbol{S(E, Y)}$ is partially differentiable with respect to thermodynamic coordinates

Let $E = E(\boldsymbol{Y})$ describe a leaf with constant S. If we displace the operational coordinates from $\boldsymbol{Y}$ to $\boldsymbol{Y} + \delta \boldsymbol{Y}$ along this leaf, the state coordinates become $(E(\boldsymbol{Y} + \delta \boldsymbol{Y}), \boldsymbol{Y} + \delta \boldsymbol{Y}))$, so we have, since S is constant on the leaf,

$$S(E(Y + \delta \boldsymbol{Y}), \boldsymbol{Y} + \delta \boldsymbol{Y}) = S(E(\boldsymbol{Y}), \boldsymbol{Y}). \tag{11.1}$$

Therefore, thanks to the partially differentiability of S with respect to E and strong differentiability of the leaf $E = E(\boldsymbol{Y})$, we have

$$S(E(\boldsymbol{Y}), \boldsymbol{Y} + \delta \boldsymbol{Y}) + \frac{\partial}{\partial E} S(E(\boldsymbol{Y}), \boldsymbol{Y} + \delta \boldsymbol{Y}) \frac{dE}{d\boldsymbol{Y}} \delta \boldsymbol{Y} = S(E(\boldsymbol{Y}), \boldsymbol{Y}). \tag{11.2}$$

That is,

$$S(E(\boldsymbol{Y}), \boldsymbol{Y} + \delta \boldsymbol{Y}) - S(E(\boldsymbol{Y}), \boldsymbol{Y}) = -\frac{\partial}{\partial E} S(E(\boldsymbol{Y}), \boldsymbol{Y} + \delta \boldsymbol{Y}) \frac{dE}{d\boldsymbol{Y}} \delta \boldsymbol{Y} = O[\delta \boldsymbol{Y}]. \tag{11.3}$$

Therefore, we conclude that $S(E, \boldsymbol{Y})$ is partial differentiable (actually, strongly differentiable) with respect to $\boldsymbol{Y}$.

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[216] The actual realizability of such a procedure will be discussed later (→**14.12**).

Thus, we may conclude that S is partial differentiable with respect to the thermodynamic coordinates.

11.5 Thermal contact in terms of adiabatic and reversible hypersurfaces

Let us consider a compound system consisting of systems I and IIthat is, as a whole, in an adiabatic condition, where each system is closed materially, and the operational coordinates of each system are fixed. Suppose heat δQ is exchanged reversibly and quasistatically between the two systems through thermal contact. For example,

$$\delta Q_{\mathrm{I}} = \delta Q, \ \ \delta Q_{\mathrm{II}} = -\delta Q. \tag{11.4}$$

For each system the change in S must be proportional to δQ (→**11.3**), so we may choose state functions θ_{I} and θ_{II} appropriately (actually, the partial derivatives of E with respect to S for each system) to write $\delta Q_{\mathrm{I}} = \theta_{\mathrm{I}}\delta S_{\mathrm{I}}$ and $\delta Q_{\mathrm{II}} = \theta_{\mathrm{II}}\delta S_{\mathrm{II}}$. Since S is extensive (→**11.3**), S of the compound system is given by $S = S_{\mathrm{I}} + S_{\mathrm{II}}$. For the compound system this change is totally internal (i.e., adiabatic) and reversible, so

$$0 = \delta S = \delta S_{\mathrm{I}} + \delta S_{\mathrm{II}} = \delta Q \left(\frac{1}{\theta_{\mathrm{I}}} - \frac{1}{\theta_{\mathrm{II}}} \right). \tag{11.5}$$

Thus, we have $\theta_{\mathrm{I}} = \theta_{\mathrm{II}}$: if two systems are in thermal equilibrium (→**7.12**), then θ's agree. Conversely, if θ's agree, then the two systems are in thermal equilibrium. If $\theta_{\mathrm{I}} < \theta_{\mathrm{II}}$, then for $\delta Q > 0$, that is, if system I obtains energy as heat and system II loses by the same amount (i.e., if system II is hotter than system I), we see[217]

$$\delta S = \delta Q \left(\frac{1}{\theta_{\mathrm{I}}} - \frac{1}{\theta_{\mathrm{II}}} \right) > 0. \tag{11.6}$$

The infinitesimal change we are considering now is an adiabatic process and pushes the state above the adiabatic and reversible hypersurface (i.e., S const surface), that is, in the direction allowed by the second law, so system I must be colder than system II (→**8.3**).

11.6 What is temperature?: absolute temperature

An intensive state quantity is called an *empirical temperature*, if it takes the same

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[217] Rigorously speaking, the following 'direct' calculation is not thermodynamically legitimate; we must connect the initial and the final equilibrium states with a reversible and quasistatic process and compute the change in S (as we will do in **14.12**). However, when the change is infinitesimal as in the present discussion, the following crude formula gives the correct result.

value between systems in thermal equilibrium and a hotter system exhibits a larger value (→**8.3**).[218] In particular, θ in **11.5** is an empirical temperature and is called the *absolute temperature*, which will henceforth be denoted by T. S will be called the *entropy* of the system.

Let dQ be the 1-form[219] expressing the amount of heat reversibly added to the system. Then, we have

$$dS = \frac{1}{T} dQ. \tag{11.7}$$

Since dS is a differential of a state function, it is an exact form (→**9.10**). Thus, T is an integrating factor of the no-exact form dQ.

Since dQ is the reversible energy change under constant operational coordinates $\boldsymbol{Y}$, we can write

$$\left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{Y}} = T \tag{11.8}$$

and regard this as the definition of the *absolute temperature*. However, since we have not chosen any unit of S, the unit of T is not determined at this point. As we will see later, if we choose the equation of state of the one-mole ideal gas as $PV \propto T$, then the T in this formula and that given by (11.8) are proportional (→**15.4**), so the choice of the proportionality constant $R = PV/T$ determines the unit of T and S (→**11.13**).

11.7 Structure of the thermodynamic space and entropy: a summary

Let us summarize the structure of the thermodynamic space which is captured analytically by the entropy S.

(1) The thermodynamic space is foliated by the adiabatic and reversible hypersurfaces on each of which entropy S is constant. These hypersurfaces are strongly differentiable (→**11.2**).

(2) Under the condition keeping all the operational coordinates constant (i.e., along a line parallel to the energy axis) entropy is a strictly monotone increasing function of E (→**11.3**), and $dS = dQ/T$, if heat dQ is added reversibly (→**11.6**).

(3) Thanks to (1) and (2) we can show (→**11.4**) that S is partial differentiable with

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[218] However, whether the existence of the so-called empirical temperature can really be empirically claimed is a delicate issue as noted in **3.8**. θ introduced here may well be the only unquestionable empirically constructed temperature.

[219] dQ is not meant to be the differential of Q, but dQ as a whole denotes a 1-form (→**9.9**). Probably writing it as q and call it a heat form may be better.

respect to the thermodynamic coordinates.
(4) Planck's principle (→**8.5**) may be restated as follows: Entropy never decreases under adiabatic conditions.

11.8 Gibbs' relation

For quasistatic processes generalized work may be expressed in terms of the generalized work form $\omega + \zeta$, so the first law of thermodynamics (→**7.14**) may be written as

$$dE = dQ + \sum_i y_i dY_i \tag{11.9}$$

in terms of operational coordinates (→**4.13**). Combining this with the entropy-reversible heat exchange relation $dQ = TdS$ (→**11.6**), we get

$$dE = TdS + \sum_i y_i dY_i. = TdS + \sum_i x_i dX_i + \sum_j \mu_j dN_j. \tag{11.10}$$

Gibbs recognized this as the fundamental relation in thermodynamics and completed the foundation of thermodynamics (→**11.9**). Thus, this relation is called *Gibbs' relation.*

The thermodynamics before Gibbs concentrated on the formulation of the second law, but Gibbs reformulated thermodynamics as an even practically useful versatile system in terms of entropy obtained by the efforts before Gibbs. The starting point of the reformulated thermodynamics is this Gibbs' relation. Each term takes the form of [an intensive quantity] multiplied by d[the corresponding (i.e., conjugate) extensive quantity].

Since entropy is the central quantity for thermodynamics, it is often natural and convenient to write Gibbs' relation for dS:

$$dS = \frac{1}{T} dE - \sum_i \frac{y_i}{T} dY_i. \tag{11.11}$$

Remark: As noted in **11.9**, Gibbs did not assume chemical reactions to occur in the system. Thus, his dN_i are operational coordinates. That is, they are materials coordinates.

11.9 Gibbs' original formulation

Here, the original passage from Gibbs' classic book[220] introducing Gibbs' relation is copied:

> (p62) Let us first consider the energy of any homogeneous part of a given mass, and its variation for any possible variation in the (p63) composition and state of this part. (By *homogeneous* is meant that the part in question is uniform throughout, not only in chemical composition, but also in physical state) If we consider the amount and kind of matter in this homogeneous mass as fixed, its energy E is a function of entropy S, and its volume V, and the differentials of these quantities are subject to the relation
>
> $$dE = TdS - PdV, \tag{11.12}$$
>
> T denoting the (absolute) temperature of the mass, and P its pressure. For TdS is the heat received, and PdV the work done, by the mass during its change of state. But if we consider the matter in the mass as variable, and write N_1, $N_2, \cdots, N_n$ for the quantities of the various substances 1, 2, $\cdots$, n of which the mass is composed, E will evidently be a function of $S, V, N_1, \cdots, N_n$, and we shall have for the complete value of differential of E
>
> $$dE = TdS - PdV + \mu_1 dN_1 + \cdots + \mu_n dN_n, \tag{11.13}$$
>
> $\mu_1, \cdots, \mu_n$ denoting the differential coefficients of E taken with respect to $N_1, \cdots, N_n$.
>
> The substances $1,\cdots,n$ of which we consider the mass composed, must of course be such that the values of the differentials $dN_1, \cdots, dN_n$ shall be independent, and shall express every possible variation in the composition of the homogeneous mass considered, including those produced by the absorption of substances different from any initially present. It may therefore be necessary to have terms in the equation relating to the component substances which do not initially occur in the homogenous mass considered, provided, of course, the substances, or their components, are to be found in some part of the whole given mass.[221]

Then, the original goes on to the phase rule (→**23.9**) discussion.
It is clear that chemical reactions are not in his scope at least in the book.

11.10 Gibbs' relation and chemical reactions

As warned in **4.11** (also noted in **11.8**) $d\boldsymbol{N}$ in $d\boldsymbol{Y}$ in this formula represents the amount of chemicals we add or remove from the system independently (operational coordinates). Therefore, due to chemical reactions (i.e., due to the shift of chemical equilibria) actual changes of the chemical composition coordinates may not be given

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[220] *The Scientific Papers of J. Willard Gibbs V1* Thermodynamics (Kessinger's Legacy Reprints version; a reprint of 1906 Longmans, Green and Co. version). Notations of the thermodynamic variables have been replaced with the corresponding ones in these notes. The page numbers referred to are those in this version.

[221] Thus, chemical reactions are totally ignored; the changes of N_i are due to (algebraic) addition only.

by $d\boldsymbol{N}$ (for example, even if we add dN_i of chemical i, in the system the amount of chemical i may not change by dN_i due to chemical reactions). The actual chemical composition changes $d\tilde{\boldsymbol{N}}$ are given by, when the ordinary thermodynamic coordinates E and $\boldsymbol{X}$ are specified,

$$d\tilde{\boldsymbol{N}} \equiv R_{E,\boldsymbol{X}}(\boldsymbol{N} + d\boldsymbol{N}) - \boldsymbol{N}, \tag{11.14}$$

where R is the reaction map (→**4.12**) giving the equilibrium composition under the condition specified by the ordinary thermodynamic coordinates E and $\boldsymbol{X}$.[222]

We can also express Gibbs' relation in terms of the chemical composition change (including the effects of chemical equilibrium shifts), i.e., $d\tilde{\boldsymbol{N}}$, as

$$dE = TdS + \sum_i x_i dX_i + \sum_j \mu_j d\tilde{N}_j. \tag{11.15}$$

This is because adding $d\boldsymbol{N}$ and adding $d\tilde{\boldsymbol{N}}$ (both as the increment of materials composition of the system) to the system result in the identical equilibrium state. Do not forget that not all the $d\tilde{\boldsymbol{N}}$ are independently changeable due to chemical equilibrium relations. The resultant materials coordinates are given by $\boldsymbol{N} + d\tilde{\boldsymbol{N}}$ or equivalently by $\boldsymbol{N} + d\boldsymbol{N}$.[223] However, the actual system energy change may still be written in terms of $d\boldsymbol{N}$ as in (11.10).

In any case, the key point is that Gibbs' relation is an exact 1-form for E with the operational coordinates as independent variables.[224,225]

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[222] Needless to say, the system before addition must be in equilibrium: $R_{E,\boldsymbol{X}}(\boldsymbol{N}) = \tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\tilde{\boldsymbol{N}})$. Here, $\tilde{\boldsymbol{N}}$ as the variable of R denotes the particular choice of the materials coordinates whose values agree with the chemical component variables.

[223] Simple illustration: consider A $\longleftrightarrow$ B with the equilibrium condition to be the identity of the amounts of A and B. Let us add δN_{A} and δN_{B} to the system. Then, obviously, $\delta \tilde{N}_{\mathrm{A}} = \delta \tilde{N}_{\mathrm{B}} = (\delta N_{\mathrm{A}} + \delta N_{\mathrm{B}})/2$.

[224] In traditional thermodynamics, the chemical composition variables are regarded as the basic chemical coordinates. However, they are not independent variables, in general, so Gibbs' relation may not be written in terms of them. For example, if $\tilde{\boldsymbol{N}}$ is fixed, in most cases, no state change can occur, because chemical equilibria depend on the internal energy and the work coordinates. Thus, we must distinguish the operational change of $\boldsymbol{N}$ and the actual change (along the actual quasistatic path) of $\tilde{\boldsymbol{N}}$ as stressed in **4.5**-**4.11**.

[225] One might introduce the so-called extent of chemical reactions (or reaction coordinates) $\boldsymbol{\xi}$ that are supposedly independent of each other by introducing appropriate catalysts. However, even if you introduce (orthogonal) reaction coordinates, still you cannot fix the reaction coordinates at your will while changing E and $\boldsymbol{X}$, because the chemical equilibria shift, meaning $\boldsymbol{\xi}$ changes.

11.11 Partial derivatives with chemical reactions

Even though $\boldsymbol{N}$ and other variables are operationally independent, as variables for description of the chemical composition of the system, $\tilde{\boldsymbol{N}}$ cannot generally be independent of other variables; you cannot fix them freely while changing E and $\boldsymbol{X}$. It is important to recall that $\tilde{\boldsymbol{N}}$ is, unfortunately, the standard thermodynamic variable in the conventional textbooks.

Gibbs' relation tells us

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},\boldsymbol{N}}, \tag{11.16}$$

but the conventional formula

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},\tilde{\boldsymbol{N}}} \tag{11.17}$$

is usually meaningless.[226] (11.16) is equivalent to

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},\mathrm{closed}}. \tag{11.18}$$

Also, we may write

$$x_i = \left(\frac{\partial E}{\partial X_i}\right)_{S,X_i^c,\boldsymbol{N}}, \tag{11.19}$$

but the conventional formula

$$x_i = \left(\frac{\partial E}{\partial X_i}\right)_{S,X_i^c,\tilde{\boldsymbol{N}}} \tag{11.20}$$

is meaningless.

We can fix S and $\boldsymbol{X}$ while changing some of the materials coordinates. Therefore,

$$\mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,\boldsymbol{X},N_i^c} \tag{11.21}$$

is meaningful, but with the chemical composition variables, an analogous expression in the standard textbooks is meaningless.[227]

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[226] To avoid this difficulty, honest textbooks explicitly demand that $\tilde{\boldsymbol{N}}$ can be fixed at our will while changing other thermodynamic coordinates. We have already noted in Remark 2 of **8.5** that this *ad hoc* convention cannot rescue chemical thermodynamics.

[227] In this 'unit' there are several statements about meaningless nature of the conventional text-

11.12 Fundamental equations

Describing a system thermodynamically involves setting up its thermodynamic space and giving its entropy S as a function of its thermodynamic coordinates $(E, \boldsymbol{Y})$. Therefore, $S = S(E, \boldsymbol{Y})$ is referred to as the *fundamental equation* of the system.

However, a fundamental equation is specific to a particular system and is not a universal function that applies to all systems. As a result, thermodynamics cannot provide it for a given system. Instead, it may be an empirical result or a product of theories outside of thermodynamics.[228]

To describe a system or a material, equations of state are often used. For example, the relation among the pressure P, volume V and temperature T for a gas is a famous example. However, since non-fundamental variables (→**3.2**) such as P and T appear, such an equation of state is insufficient to determine the fundamental equation; we need knowledge of E. Let us see the problem for an ideal gas (→**11.13**).

11.13 Fundamental equation of ideal gases

The relation between pressure P, volume V and temperature T for an N mole ideal gas is usually called the equation of state of an ideal gas:

$$PV = NRT. \tag{11.22}$$

Here, R is the gas constant.[229] This relation is, like all other equations of state, not a result of thermodynamics, but a result of experiments or some other theories.

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book expressions. However, we must note that not all the textbooks are imprecise. For example, Kirkwood and Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, 1961) clearly states that the usual Gibbs' formula for open systems applies when there is no chemical reaction (p52 for homogeneous systems, p56 for inhomogeneous systems). It is also stated clearly on p48 that, for a closed system, the changes due to chemical components do not appear at all in the expression of the first law.

However, on p101 we find the following statement: 'In a closed system in which the masses of the components are changed,

$$dE = TdS - PdV + \sum \mu dN \tag{8.4}$$

From this the chemical equilibrium condition under constant S and V is discussed. Thus, clearly there is a confusion.

[228] For example, if thermodynamics is applied to chemical industry, almost always detailed experimental data are used, while detailed steam tables (e.g., found in this) are employed for steam engines.

[229] $R = 8.314\,462\,618\,153\,24\ \mathrm{m^2{\cdot}kg/s^2{\cdot}K{\cdot}mol}$.

To describe an ideal gas thermodynamically, we must first set up its thermodynamic space, and then provide its entropy as a function of thermodynamic coordinates or give its internal energy as a function of entropy and operational coordinates.

For an ordinary gas with a fixed amount its thermodynamic coordinates are only V in addition to E. Therefore, its fundamental equation takes the form: $S = S(E, V)$, which is not provided by thermodynamics, but requires empirical data. One such piece of data is the so-called equation of state (11.22), while the other is a relation between E and some other variables (called a *thermal equation of state*). For an ideal gas, we use the 'fact' that E depends only on T linearly.

If we heat the gas without any work, all the added heat would be converted to the internal energy. Thus, under constant volume (i.e., the work coordinate constant), we assume (based on empirical results)

$$E = C_V T, \tag{11.23}$$

where C_V is a constant (later called the constant volume heat capacity →**14.6**). Gibbs' relation (→**11.8**)

$$dS = \frac{1}{T}dE + \frac{P}{T}dV \tag{11.24}$$

and (11.23) tell us that under a constant volume condition

$$dS = \frac{C_V}{E}dE. \tag{11.25}$$

Since entropy is a state quantity, dS is exact (→**9.10**). Therefore, the entropy of an equilibrium state F $= (E, V)$ is obtained from that of the initial state I $= (E_0, V_0)$ by any process described by any continuous curve[230] connecting I and F (→**9.14**). Therefore, let us line integrate (11.24) along the path first going from I to state M $= (E, V_0)$ and then from M to F (Fig. 11.1). For a 1 mole gas $P/T = R/V$, so the fundamental equation for a 1 mole ideal gas reads

$$S = S_0 + \int_{E_0}^{E} \frac{C_V}{E}dE + \int_{V_0}^{V} \frac{R}{V}dV = S_0 + C_V \log\frac{E}{E_0} + R\log\frac{V}{V_0}. \tag{11.26}$$

From this, we can get everything we wish to know thermodynamically:

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E = \frac{R}{V}, \quad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{C_V}{E}. \tag{11.27}$$

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[230] Actually, 'continuity' alone is inconvenient, so throughout these lectures, we assume that the curve has a length (→**9.14**).

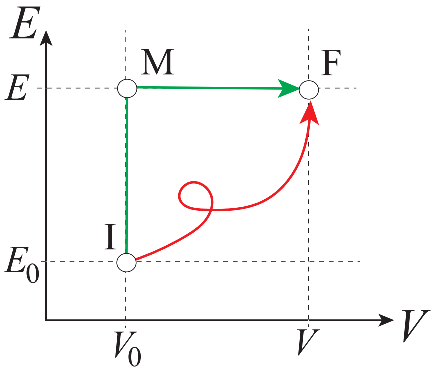

Figure 11.1: The green path is the integration path for (11.26). We may use any curve (say, the red curve) connecting I and F in the thermodynamic space, but a practical path must be something like the green one.

12 Principle of increasing entropy

12.1 How to make various non-homogeneous equilibrium states

We have seen in **5.8** that we can prepare an equilibrium state of a compound system (→**2.9**) by combining simple systems in equilibrium through various walls (boundary conditions →**2.1**) and then leave it for a sufficiently long time in a fixed environment that does not cause any dissipation even after any time dependence subsides. Here, a wall (= boundary condition) is specified by a set of extensive quantities allowed to be exchanged across it.

In thermodynamics, only equilibrium systems that can be constructed as described in the preceding paragraph are discussed. Note that the component simple systems appearing in the construction of a compound system can be macroscopically (→**1.4**) extremely small. Thus, as stages for the usual macrophysics (fluid dynamics, rheology, etc.) such compound systems provide sufficiently detailed macroscopic description of a system.[231]

12.2 Constrained equilibrium states

If we remove all the walls between any simple subsystems defining a compound system (→**12.1**) in equilibrium (i.e., if all the boundary constraints on intrasystem exchanges of extensive quantities are abolished), the system would eventually settle down to an equilibrium state of a simple system.[232]

Since the system as a whole was in equilibrium[233] even before abolishing walls, the original system should be regarded as in an equilibrium state but is not allowed to reach the unconstrained equilibrium state by constraints (walls). Therefore, let us call the original equilibrium state of the compound system a *constrained equilibrium state*. Since all the walls need not be abolished at once, there are many different constrained equilibrium states for a given (compound) system.

To (partially) remove constraints may be expressed as reducing or weakening the constraints.

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[231] Needless to say, this does not mean in fluid dynamics, rheology, etc., small macroscopic parts of a system are in equilibrium.

[232] Usually; always, especially if all the component simple systems are made of the same chemical components.

[233] According to our definition of 'equilibrium' **2.7**.

The devices imposing constraints (in many cases walls) themselves do not contribute thermodynamic quantities to the system; they exert thermodynamic effects only through interfering the exchange of extensive quantities. Therefore, as stated before, such devices (walls) are very often identified with particular mathematical boundary conditions imposed there.[234]

12.3 The principle of increasing entropy

Suppose an equilibrium state of an adiabatic (in particular, isolated) system spontaneously changes into another equilibrium state (e.g., after reducing constraints →**12.2**). The system entropy can never decrease by this change. This is called the *principle of increasing entropy.*[235] This is because we can never go below the initial reversible adiabatic hypersurface adiabatically (→Fig. 10.2). If you wish to decrease entropy, you must cool the system (→**11.7**(3)).

This logic tells us, more generally, that the system entropy never decreases with the process of relaxing the constraints under an adiabatic condition. In a closed system under an adiabatic condition, if a change occurs spontaneously from an initial to a final equilibrium state, the system entropy can never decrease.

However, this only means that if the initial entropy and that of the final equilibrium state is compared, the latter cannot be smaller. Even if we say the entropy increases with a process through relaxing constraints, it does not mean the system entropy at any time point increases during the process. Do not forget that entropy is defined only for equilibrium states.[236]

---

[234] Needless to say, this identification is allowed only when (sub)systems are macroscopic. Nowadays, systems with a very few microscopic particles or microscopic mechanical degrees of freedom are discussed as thermodynamic systems, and their boundaries are often mathematical boundary conditions. Whether such an idealization is meaningful or not should be critically considered case by case.

[235] ⟪**$\Delta S > 0$ shown?**⟫ Note that what is actually demonstrated up to this point is only $\Delta S \not< 0$; that is, we have only demonstrated that, if $\Delta S < 0$, then the second law would be violated. $\Delta S > 0$ has never been demonstrated, so, logically speaking, 'increasing' is an exaggeration. However, *within the thermodynamic framework*, we have examples in which actually $\Delta S > 0$ can be demonstrated under the condition for $\Delta S \not< 0$, so it is admissible to use this name for the principle.

The situation is quite different from the so-called pure mechanical demonstration of the second law (e.g., using Jarzynski's inequality).

[236] Thus, it is meaningless to mention the thermodynamic entropy of the universe.

12.4 The entropy maximizing principle

Due to **12.3**, if the entropy of a closed adiabatic system becomes maximum under given constraints, the system cannot change any further, so the system is in (constrained) equilibrium.[237]

The converse also holds under the metaprinciple of thermodynamics (→**8.4**). If the system entropy is not max, then there is no thermodynamic proposition (or principle) that is violated even if a spontaneous change happens to increase its entropy. Therefore, the system cannot be in equilibrium. Thus, 'entropy max' and 'equilibrium' are equivalent. This is called the *maximum entropy principle* or *entropy maximizing principle*.

Since the metaprinciple **8.4** is used, in practice, what thermodynamics tells us is that it does not concern whether the maximum principle actually holds or not; in contrast, the principle of increasing entropy demands an increase (precisely, non-decrease; see a footnote in **12.3**).

12.5 Entropy max does not imply entropy extremum

Even if a system is in equilibrium, its entropy need not be maximum due to entropy being extremal. This is simply because the maximum of a continuous function occurs at an extremum or at the domain boundary (see, for an example, **16.6**).

12.6 Thermodynamic variations

Variations of a thermodynamic state of a system are not simple displacements of the corresponding point in the thermodynamic state of the system.

A thermodynamic variation is specified by a partition $\mathcal{P}$ into macroscopic pieces of the system under study. The thermodynamic coordinates of macroscopic subsystems are chosen under the condition that the total extensive quantities of these subsystems agrees with the original total amounts.[238] The boundary conditions between subsystems may be chosen appropriately so that the state of the resultant compound system can stay in equilibrium (in order to use thermodynamics). Unless otherwise stated, the walls (boundary conditions) in the original compound systems

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[237] Here, the uniqueness of the state with max entropy may not always be true. However, the change of one state to another with the same entropy does not usually occur spontaneously in a macroscopic system (within a short time).

[238] If you wish to consider non-additive extensive quantities, the combined extensive quantities must be consistent with the amount in the original state as noted in the next footnote.

are kept and the imposed constraints are respected when thermodynamic variations are constructed (Fig. 12.1).

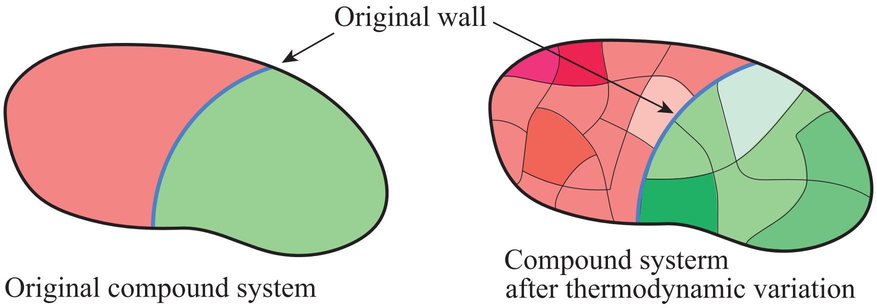

Figure 12.1: Unless otherwise stated, the walls (boundary conditions) in the original compound systems are kept and the imposed constraints are respected when thermodynamic variations are constructed.

For a function of thermodynamic coordinates $J(E, \boldsymbol{Y})$, its variation δJ due to the given thermodynamic variation is computed as

$$\delta J(E, \boldsymbol{Y}) = \sum_{i \in \mathcal{P}} J(E_i, \boldsymbol{Y}_i) - J(E, \boldsymbol{Y}), \tag{12.1}$$

where $\mathcal{P}$ denotes the set of subsystems by a particular partition of the original system into subsystems, $E = \sum_{i \in \mathcal{P}} E_i$ and $\boldsymbol{Y} = \sum_{i \in \mathcal{P}} \boldsymbol{Y}_i$.[239] That is, a *thermodynamic perturbation* is defined by a particular spatial partition $\mathcal{P}$ (with appropriate boundary conditions and a particular distribution of thermodynamic coordinates $\{E_i\}$ and $\{\boldsymbol{Y}_i\}$).

The quantities with δ are often called virtual variations. This means that we do not worry too much about actual realizability of the variations. Here, δ does not mean that the variation is small in any sense. Still, we can say a thermodynamic perturbation δ is small if the thermodynamic densities (→**5.5**) change only slightly.

Remark. δJ above is *not* defined as the difference between the original state and any result after modification. It is defined by comparing two equilibrium states, the original state that is in equilibrium and the final *equilibrium* state that the system reaches in a sufficiently long time after modification/variation is applied. All thermodynamic perturbation results are not simple variations due to perturbative operations

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[239] If there are work coordinates that are not additive, then the choice of the values for each piece is complicated, but still we may assume the distribution of variables compatible with $\mathcal{P}$ is possible.

but the variations eventually realized after the system subjected the operations to equilibrates.

12.7 Variational principle given by the second law

For an equilibrium state of a system, if there were a thermodynamic variation for which $\Delta S > 0$, then there would be an equilibrium state with larger entropy. Therefore, the entropy maximization principle (→**12.4**) tells us that the original equilibrium state was not a true equilibrium state of the system. In other words, for any thermodynamic variation, any equilibrium state must satisfy:

$$\Delta S \leq 0. \tag{12.2}$$

Traditionally, (12.2) is called the (thermodynamic) *stability criterion* of an equilibrium state, but as the derivation tells us, it is a universal property of any equilibrium system.[240]

For a compound system, if the internal constraints due to the walls (internal boundary conditions) may be removed, then there may be a thermodynamic variation with $\Delta S > 0$. In this case, the original equilibrium state is no longer an equilibrium state after removing (some of) the internal constraints, and the system can spontaneously evolve to a new equilibrium state with a larger entropy. Thus,

$$\Delta S > 0 \quad \Longleftrightarrow \quad \text{the state can spontaneously evolve to a new equilibrium state} \tag{12.3}$$

may be called the *evolution criterion* for an equilibrium state under an adiabatic condition (after relaxing the constraints).[241]

---

[240] As we will learn soon, it is equivalent to $-S$ being convex. See **13.5**.

[241] As noted in **12.4**, the evolution criterion is often true, but whether the change actually happens or not is, strictly speaking, beyond the power of thermodynamics; if thermodynamics forbids, even God cannot disobey, but what thermodynamics allows may not happen easily (can be realized by God).

13 Convexity and principle of minimizing internal energy

13.1 Convex analysis and thermodynamics

We have seen that the thermodynamic space of a system is a Euclidean space spanned by the internal energy E and the operational coordinates $\{Y_i\}$ (→**11.7**). The thermodynamic space is (trivially) foliated by reversible adiabatic hypersurfaces on which entropy is constant. If a certain point in $\mathcal{E}$ (= a certain thermodynamic state) is given, its entropy is determined as a state quantity by the fundamental equation (→**11.12**). Or, if the operational coordinates and entropy S are fixed, the internal energy of the system is determined, so internal energy is given as a state function of S and operational coordinates as $E = E(S, \boldsymbol{Y})$.

As we will see soon, E and S (precisely, $-S$) are (under certain reservations but substantially[242]) convex functions. Convexity imposes strong constraints on the mathematical structure of thermodynamics. For example, a convex function is a C^1-function if it is strongly differentiable. This implies that absolute temperature is continuous with respect to operational coordinates.[243]

The subfield of analysis discussing convex functions is called *convex analysis*. It is highly desirable that any physicist has rudimentary knowledge of convex analysis, but it is not covered by the standard math courses for physics students. In this set of lecture notes, convex functions are defined in this section with some of their elementary properties explained. Other crucially important topics on convex analysis will be discussed later in Section 18.

13.2 Epigraph and convex function

Let us write a function f with n independent variables $x_1, \cdots, x_n$ as $y = f(\mu)$ $(\mu = (x_1, \cdots, x_n))$.[244] Then, the *graph* of f is, if continuous, a n-hypersurface in

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[242] If there is no non-additive work coordinates

[243] However, do not forget that T may not be differentiable, if it is considered as a function of the variables other than the thermodynamic coordinates.

If chemicals are described in the conventional fashion as in the textbooks, then we cannot thermodynamically claim that chemical potentials are continuous as functions of thermodynamic coordinates.

[244] The domain of f is assumed to be convex. In standard textbooks of convex analysis such as Rockafellar's *Convex Analysis* for any function f its value outside its usual domain is set $f = +\infty$

$n+1$ space (y,μ) any of whose point is at the height y at position μ in the n-hyperplane $(0,\mu)$. The point set above this graph including the graph is called the *epigraph* of function f (Fig. 13.1). More precisely:

Let C be the domain of f. Its epigraph epi f is defined by

$$\text{epi}\, f = \{(y,\mu)\,|\, y \geq f(\mu), \mu \in C\}$$

Note the equality sign in $y \geq f(\mu)$ in the definition.

A function f defined on a convex set (→**5.10**) whose epigraph epi f is a convex set is called a *convex function*.

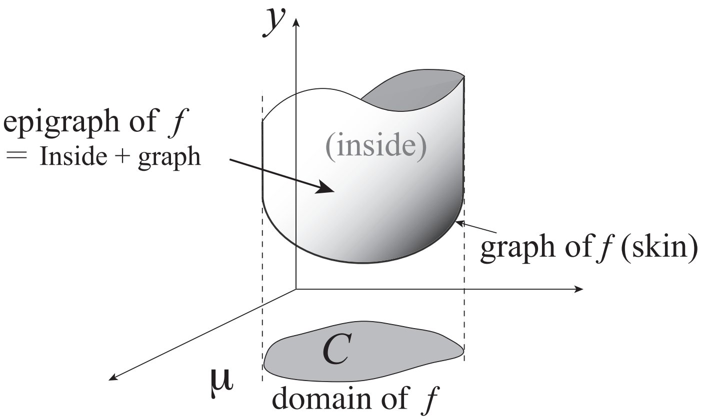

Figure 13.1: An epigraph and the corresponding convex function

A function that is convex upward is called a *concave function*. Convex functions are convex downward in mathematics.

13.3 Jensen's inequality

A crucial inequality for convex functions is:

Theorem [Jensen's inequality]

For a function $f : C \mapsto \mathbb{R}$ to be a convex function a necessary and sufficient condition is

$$f\left(\sum_i \lambda_i \mu_i\right) \leq \sum_i \lambda_i f(\mu_i), \tag{13.1}$$

---

and its domain is extended to the whole space. Here, we will not use this convention which is standard for convex analysis, but adopt the usual convention for functions. This will not be stated explicitly.

where $\lambda_i \geq 0$ and $\sum_i \lambda_i = 1$. This inequality is called *Jensen's inequality*. In other words, if we write a general weighted average as $\langle\ \rangle$

$$f(\langle\mu\rangle) \leq \langle f(\mu)\rangle \tag{13.2}$$

is a necessary and sufficient condition for f to be a convex function. Its meaning should be clear from the following Fig. 13.2 (for two variables $\mu = (x_1, x_2)$).

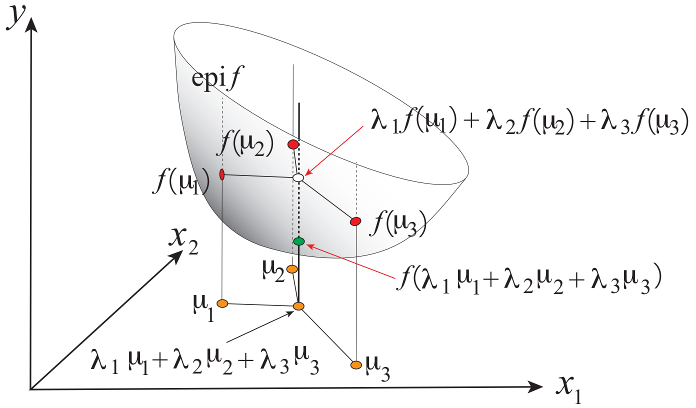

Figure 13.2: A convex function with two independent variables; Jensen's inequality (in this illustration for three points) means that the green dot on the graph is below the white dot (inside the epigraph).

13.4 Analytic properties of convex functions

Some important properties of a convex function are summarized without proof.

(1) A convex function is Lipshitz continuous.[245]

(2) A convex function is directionally continuously differentiable (→**9.1**) along any line in its domain except for countably many points.

(3) A convex function is continuously differentiable at a point where it is strongly differentiable (→**9.3**).

13.5 Entropy is a concave state function

Consider two equilibrium systems 1 and 2 whose thermodynamic coordinates are $(E_1, \boldsymbol{Y}_1)$ and $(E_2, \boldsymbol{Y}_2)$, respectively. Both states are assumed to be in the same set of equilibrium states $\mathcal{E}$ of a simple system. From these two systems we make a

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[245] $f(x)$ is Lipshitz continuous at x, if in a neighborhood of x we can choose a positive number K such that $|f(x) - f(y)| < K|x - y|$. For the ordinary continuity, no bound for K is required.

compound system, and then remove the wall between 1 and 2. The entropy before removing the isolating wall the entropy of the compound system is

$$S(E_1, \boldsymbol{Y}_1) + S(E_2, \boldsymbol{Y}_2). \tag{13.3}$$

After removing the wall constraints, if work coordinates satisfy additivity,[246] the entropy of the resultant combined system is $S(E_1 + E_2, \boldsymbol{Y}_1 + \boldsymbol{Y}_2)$. According to the principle of increasing entropy (→**12.3**) we have

$$S(E_1 + E_2, \boldsymbol{Y}_1 + \boldsymbol{Y}_2) \geq S(E_1, \boldsymbol{Y}_1) + S(E_2, \boldsymbol{Y}_2). \tag{13.4}$$

If we apply the extensivity of entropy (→**11.3**) for $\lambda \in [0, 1]$

$$\lambda S(E, \boldsymbol{Y}) = S(\lambda E, \lambda \boldsymbol{Y}), \tag{13.5}$$

so, combining the two relations, we get

$$S(\lambda E_1 + (1-\lambda)E_2, \lambda \boldsymbol{Y}_1 + (1-\lambda)\boldsymbol{Y}_2) \geq \lambda S(E_1, \boldsymbol{Y}_1) + (1-\lambda)S(E_2, \boldsymbol{Y}_2). \tag{13.6}$$

That is, $-S$ is a convex function according to the theorem in **13.3**; in other words, S is a concave function.[247]

If we wish to extend the above convexity argument to compound systems, we assume two systems are with the identical internal constraints (walls/boundary conditions), and when two systems are combined, we assume that the choice of the two states respect the constraints and the combination is realized between the corresponding pieces of the subsystems defining the compound systems (schematically illustrated in Fig. 13.3). Then, an inequality analogous to (13.6) holds.

13.6 The so-called stability criterion $\delta S > 0$ and convex analysis

We have shown for any equilibrium state its entropy increases by any thermodynamic variation in **12.7**. It is copied here for convenience:

$$\Delta S \leq 0. \tag{13.7}$$

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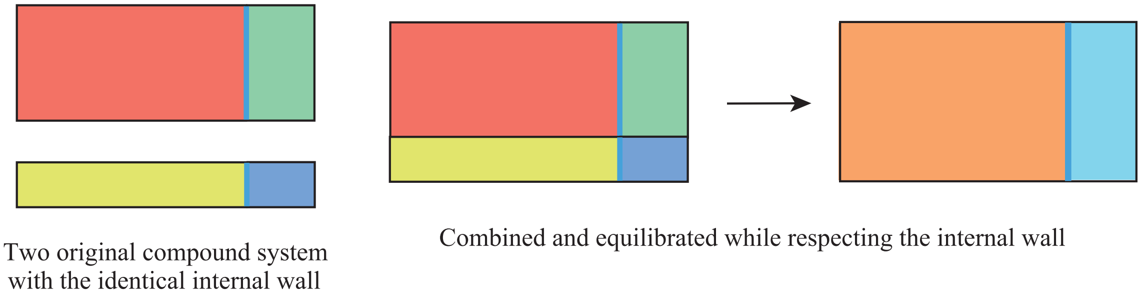
[246] Note that partition additivity (→**2.13**) is not enough.

[247] **Warning**. With the conventional expression of chemicals entropy is not a concave function. Following the *ad hoc* convention of freely freezing chemical reactions, while reactions are frozen, entropy is concave.



Two original compound system with the identical internal wall

Combined and equilibrated while respecting the internal wall

Figure 13.3: Convex combinations of compound systems must respect internal boundary conditions a schematically illustrated here.

First of all notice that this inequality is simply Jensen's inequality applied to $-S$, since $-S$ is convex. As remarked just below (12.2), its the property of any equilibrium state. Convex analysis confirms this statement for simple systems.

For a compound system, (13.7) holds, if all the original internal constraints (walls/boundary conditions) in the system are respected when thermodynamic variations are constructed. Here, we assume that any imposed thermodynamic variation never alters the internal constraints (if any for compound systems). Then, again, (13.7) is a convexity result that is due to the nature of entropy.

13.7 Entropy is C^1 with respect to thermodynamic coordinates

We have demonstrated that $S(E, \boldsymbol{Y})$ is partially differentiable (→**11.4**) concave function. This and **13.4** (2) imply that all the partial derivatives are continuous. Therefore, The theorem shown in **9.4** implies that $S(E, \boldsymbol{Y})$ is strongly differentiable.[248] Thus, we may conclude that entropy as a function of thermodynamic coordinates is strongly and continuously differentiable.

Consequently, conjugate intensive variables (the so-called thermodynamic fields →**5.5**) are all continuous functions of thermodynamic coordinates. In particular, temperature and chemical potentials are continuous functions of thermodynamic coordinates.[249]

13.8 The inverse function of a monotone decreasing convex function is

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[248] Since we did not show previously that $S(E, \boldsymbol{Y})$ is strongly differentiable, we cannot use **13.4** (3).

[249] Here, the continuities here are shown only when the independent variables are the thermodynamic coordinates or those with E being replaced by S.

also a monotone decreasing convex function

Let x and y be reals and $y = f(x, Z)$ be a convex function defined on $C \subset \mathbb{R} \times \mathbb{R}^n$. Furthermore, we assume for each $Z \in \mathbb{R}^n$ f is a strictly monotone decreasing function of $x \in \mathbb{R}$ (that is, $x_1 < x_2 \Rightarrow f(x_1, Z) > f(x_2, Z)$). At each Z we can uniquely solve $y = f(x, Z)$ for x, so we can define the function $x = g(y, Z)$ on $(y, Z) \in f(C) \times \mathbb{R}^n$. The resultant g is convex. This assertion should be clear from the following illustration Fig. 13.4:

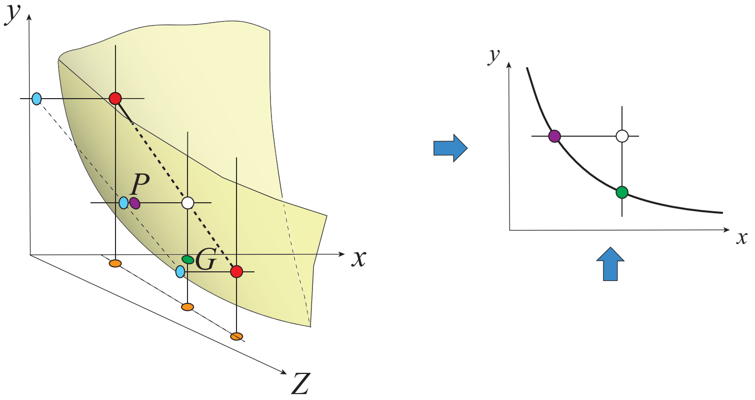

Figure 13.4: A strictly decreasing convex function with respect to one coordinate: Red dots (green and purple dots also) are on the graph of the function (the yellow surface). Jensen's inequality is illustrated by the white dot above green dot G or right of purple dot P. The blue dots are on the yZ hyperplane and the orange on the xZ-hyperplane. The essence may be exhausted by the right diagram, exhibiting, "The inverse function of strictly decreasing convex function is also a strictly decreasing convex function"; the graph seen along either arrow is convex.

13.9 Internal energy is convex

13.5 tells us that $-S = -S(E, \boldsymbol{Y})$ is a convex function, and when $\boldsymbol{Y}$ is fixed, $-S$ is strictly decreasing function of E, since its derivative is $-1/T < 0$. Therefore, as shown in **13.8**, E is convex as a function of $(-S, \boldsymbol{Y})$. Thus,[250] $E = E(S, \boldsymbol{Y})$ is convex.

13.10 Internal energy minimization principle

Since E is convex, combining systems I and II in equilibrium to make a new system

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[250] For example, if $y = f(x)$ is convex, then on the same region $y = f(-x)$ (the mirror image with respect to the plane perpendicular to x) is convex as well.

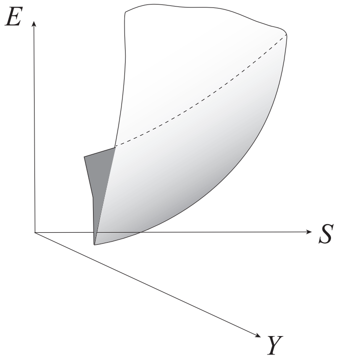

Figure 13.5: $-S$ is a strictly decreasing convex function of E when $\boldsymbol{Y}$ is fixed, so E is a convex function of $(S, \boldsymbol{Y})$.

(by relaxing some constraints between I and II), we have an analogous inequality (i.e., Jensen's inequality for E) as (13.6)

$$E(\lambda S_1 + (1-\lambda)S_2, \lambda \boldsymbol{Y}_1 + (1-\lambda)\boldsymbol{Y}_2) \le \lambda E(S_1, \boldsymbol{Y}_1) + (1-\lambda)E(S_2, \boldsymbol{Y}_2). \quad (13.8)$$

In particular, if we apply a thermodynamic variation (→**12.6**), since E is convex, we have

$$\delta E \ge 0. \quad (13.9)$$

This is a universal property of the internal energy of any equilibrium state under any thermodynamic variation just as the counterpart for entropy already discussed in **13.6**.

13.11 Continuous strong differentiability of internal energy and entropy

We know S is continuously (strong) differentiable with respect to the thermodynamic coordinates (→**13.7**). An analogous argument shows that E is continuously (strong) differentiable with respect to S and work coordinates.

Haven't the conjugate variables of the work coordinates been introduced from outside thermodynamics, due to the nonthermal macrophysics? Why, then, are their properties constrained by thermodynamics? One way to understand the situation is that thermodynamics does not alter the properties of conjugate variables, but the systems that do not have continuous conjugate variables do not realize proper equilibrium states for which thermodynamics holds or some members of the thermodynamic coordinates are not additive.

14 Heat and entropy

14.1 Entropy: summary

Let us summarize the properties of entropy S.
(1) The thermodynamic space is foliated by strongly differentiable hypersurfaces defined by reversible adiabatic accessibility (→**11.7** for a summary) on which entropy is constant.
(2) Entropy is a continuously (strongly) differentiable concave function of the internal energy and operational coordinates $\boldsymbol{Y}$ (→**11.3**). This implies that the internal energy is a continuously (strongly) differentiable convex function of S and $\boldsymbol{Y}$ (→**??**).
(3) If we add heat $q = dQ$ quasistatically to the system under constant work coordinates without material exchanges (that is, while keeping all the operational coordinates constant), the system entropy changes by $dS = dQ/T$ (→**11.6**). Consequently, the differential form for the first law of thermodynamics may be written as Gibbs' relation: $dE = TdS + \sum ydY$ (→**11.8**).
(4) Planck's principle implies that entropy can never decrease under adiabatic conditions. This leads to the principle of increasing entropy **12.3**.

14.2 Heat bath and heat exchange

A system is called a *heat bath*, if it is in thermal contact (→**7.12**) with a system and is kept at a constant temperature (→**8.8**). Note, however, that even if a system is in contact with a single heat bath, if there is no net exchange of heat with it, the system is adiabatic.

If a heat bath of temperature T_B exports energy Q (> 0) as heat, the entropy of the heat bath decreases by Q/T_B:

$$\Delta S_{\text{bath}} = -\frac{Q}{T_B}. \tag{14.1}$$

If energy $|Q|$ is released by the system to the heat bath, that is, if the system gains heat Q (< 0) from the heat bath, the heat bath gains heat $-Q$ (> 0) from the system, so (14.1) can always be used with the sign of Q understood algebraically.

14.3 The existence of intrinsic heat bath

Suppose a system is in equilibrium. Is there any heat bath that does not change the system state even when in thermal contact with it? In other words, is there always a heat bath that is in thermal equilibrium with a given equilibrium system?

For a system in equilibrium, we can define its temperature. The concavity of entropy and its differentiability implies temperature is a continuous quantity (→**13.7**), so there must be a heat bath at the same temperature of a given system. Let us call such a heat bath an *intrinsic heat bath* of the system. In particular, even if a system is in thermal contact with its intrinsic heat bath, the system state does not change. Even if the system is adiabatic before this thermal contact, its state does not change.

The existence of the intrinsic heat bath eloquently tells us that thermodynamic equilibrium states cannot be described as a system described in terms of mechanics and electrodynamics of the system alone in general.[251]

14.4 Clausius' inequality

Suppose a system is in thermal contact with a heat bath of temperature T_B, and the compound system consisting of the system and the heat bath as a whole is under adiabatic conditions. If energy Q is transferred as heat from the heat bath to the system and if the whole system reaches an equilibrium, (14.1) tells us that the total entropy change ΔS_{total} is given by

$$\Delta S_{\text{total}} = \Delta S - \frac{Q}{T_B}, \tag{14.2}$$

where ΔS is the system entropy change. Since the whole system is adiabatic, the total entropy cannot decrease (the principle of increasing entropy→**12.3**), so we must have $\Delta S_{\text{total}} \geq 0$. Consequently,

$$\Delta S \geq \frac{Q}{T_B}. \tag{14.3}$$

This is called *Clausius' inequality.* Here, note that the temperature in the inequality is not the system temperature (though it is the final temperature of the system)

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[251] Can a system in thermodynamic equilibrium be fully described solely in terms of pure mechanics? Statistical mechanics assumes it is possible, but it is crucial for the reader to understand that despite being called statistical "mechanics," this framework does not actually rely on mechanics (be it classical, quantum, or any other form). For instance, it does not require the fundamental element of mechanics: equations of motion. From an empirical science perspective, it remains unknown whether a many-body system truly follows mechanics.

14.5 More general Clausius' inequality

Suppose a system is in thermal contact with more than one heat bath and obtains heat Q_i from heat bath i at temperature T_i.[252] If the system and all the heat baths are collectively under adiabatic conditions, the total entropy change may be written as (cf. (14.2))

$$\Delta S_{\text{total}} = \Delta S - \sum_i \frac{Q_i}{T_i}. \tag{14.4}$$

During the process the system can do work as long as the whole system is adiabatic. Again, the principle of increasing entropy (→**12.3**) implies

$$\Delta S \geq \sum_i \frac{Q_i}{T_i}. \tag{14.5}$$

This is also called Clausius' inequality. For the equality to hold, the heat exchange with each heat bath must be quasistatic, so the system temperature must be adjusted each time it exchanges heat with different heat baths (as in **15.1**).

For any cycle for the system (a process whose intial and final system states are identical), since entropy is a state quantity, (14.5) becomes

$$0 \geq \sum_i \frac{Q_i}{T_i}. \tag{14.6}$$

The equation equivalent to this was derived by Clausius before he reached the entropy concept (→**A.13**).

14.6 Heat capacity

For simplicity, let us consider a system with a single temperature in equilibrium. We add heat δQ reversibly and quasistatically (under a certain condition), and the system temperature changes as $T \to T + \delta T$. The proportionality constant $C(T)$ (which may depend on T) in the following formula:

$$\delta Q = C(T)\delta T \tag{14.7}$$

is called the *heat capacity* of the system (under a specific condition at temperature T).

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[252] The contacts with various heat baths may be simultaneous, allowing heat transfer from a heat bath to another via the system. What matters here is the total amount of heat (net heat) Q_i for each bath i, which maintains equilibrium.

There are many heat capacities under various conditions (e.g., under constant volume). The condition 'cond' is attached as C_V for the capacity under constant volume condition.

The amount of required heat causing a uniform change in a system scales with the system volume (or mass), so the heat capacity is an extensive quantity.

If heat is added reversibly (→**14.10**), then δQ may be written in terms of entropy. Therefore, generally we may write (if S is differentiable with T[253])

$$C_{\rm cond}(T) = T\left(\frac{\partial S}{\partial T}\right)_{\rm cond}. \tag{14.8}$$

However, no entropy is needed to define the heat capacity.

14.7 The relation between internal energy and heat capacity

If we apply Gibbs' relation to (14.8), generally, we have,

$$C_{\rm cond}(T) = \left(\frac{\partial E}{\partial T}\right)_{\rm cond} - \sum_i y_i \left(\frac{\partial Y_i}{\partial T}\right)_{\rm cond}. \tag{14.9}$$

The chain rule gives (here, Y_i^C implies that only Y_i is removed from $\boldsymbol{Y} = \{Y_i\}$)[254]

$$\left(\frac{\partial E}{\partial T}\right)_{\rm cond} = \left(\frac{\partial E}{\partial T}\right)_{\boldsymbol{Y}} + \sum_i \left(\frac{\partial E}{\partial Y_i}\right)_{{\rm cond},Y_i^c} \left(\frac{\partial Y_i}{\partial T}\right)_{\rm cond}, \tag{14.10}$$

so we have[255]

$$C_{\rm cond}(T) = \left(\frac{\partial E}{\partial T}\right)_{\boldsymbol{Y}} + \sum_i \left\{\left(\frac{\partial E}{\partial Y_i}\right)_{{\rm cond},Y_i^c} - y_i\right\} \left(\frac{\partial Y_i}{\partial T}\right)_{\rm cond}. \tag{14.11}$$

If the thermodynamic coordinates are only E and V as for the ordinary gas, (14.11) gives

$$C_P = C_V + \left\{\left(\frac{\partial E}{\partial V}\right)_P + P\right\} \left(\frac{\partial V}{\partial T}\right)_P. \tag{14.12}$$

---

[253] Remember that the strong differentiability of S is guranteed only for thermodynamic coordinates (→**13.7**).

[254] If the condition includes some Y_i, the derivative with 'cond, Y_i^c' should be removed or set 0.

[255] Note that if the conventional chemical coordinates—the chemical composition variables $\tilde{\boldsymbol{N}}$—are used as the usual thermodynamic textbooks, the corresponding formula becomes complicated.

For an ideal gas (→**11.13**) the internal energy E is a function of T, and for 1 mole of an ideal gas $PV = RT$, so the above formula reduces to Mayer's relation (→**14.8**):

$$C_P = C_V + R. \tag{14.13}$$

Here, C_P and C_V are constant pressure and constant volume molar specific heat, respectively.

14.8 Mayer's relation

(14.13) was the relation used by Mayer to determine the work equivalent of heat (→**A.9**). Needless to say, however, the relation was not derived with the aid of thermodynamics, but by using *Mayer's cycle* illustrated in Fig. 14.1. Here, one mole of an ideal gas is used.

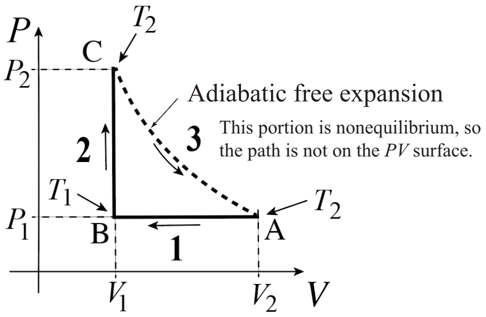

Figure 14.1: Mayer's cycle

Fig. 14.1 Mayer's cycle consists of three processes: Reversible and quasistatic compression under constant pressure **1**, reversible and quasistatic heating under constant volume **2**, and adiabatic free expansion **3**. Mayer knew Gay-Lussac's 'law of constant temperature': no temperature changes under adiabatic free expansion.

The gas does not do any work and adiabatic during Process **3** in Fig. 14.1, so its internal energy is constant. During Process **1** the system is compressed under constant pressure, and energy is obtained by the system as work::

$$W = P_1(V_2 - V_1) = R(T_2 - T_1) > 0. \tag{14.14}$$

During this process the system temperature goes down from T_2 to T_1 under constant pressure so the system obtains negative heat Q_1:

$$Q_1 = C_P(T_1 - T_2) < 0. \tag{14.15}$$

Process **2** is heating under constant volume, and the system absorbs heat Q_2:

$$Q_2 = C_V(T_2 - T_1) > 0. \tag{14.16}$$

After one cycle, the system must return to the original state, so the internal energy must return to its original value:

$$W + Q_1 + Q_2 = 0 \;\Rightarrow\; R(T_2 - T_1) + C_P(T_1 - T_2) + C_V(T_2 - T_1) = 0. \tag{14.17}$$

Thus, Mayer's relation (14.13) has been obtained.

$Q_1 + Q_2$ may be thermally measured and W can be mechanically obtained, so the conversion factor of the unit of heat cal and unit of work J, that is, the work equivalent of heat cal/J should be determined.

The data for Mayer's original computation in 1842 were:

$C_P = 0.267$ cal/g·deg, the specific heat ratio $\gamma = C_P/C_V = 1.421$ and the thermal expansion coefficient $\alpha = 1/274\ \mathrm{K}^{-1}$ to compute the volume expansion.

From these values we can obtain cal/J=3.59. Get this number, using the gas of 1 cm^3; Mayer adopted the mass of the 1 cm^3 gas to be 0.0013 g, and the pressure to be 1 atm: $P = 1033 \times 980$ dyn/cm^2 (Answer[256]).

14.9 "Emden's problem"

Suppose a leaky room of volume V is maintained at pressure P as the outside. If air is regarded as an ideal gas $PV = NRT$, and $E = NC_VT$ hold, so the following ratio is constant (the constant volume specific heat of diatomic ideal gas is $5R/2$):

$$E/PV = C_V/R = 5/2. \tag{14.22}$$

Since this ratio does not depend on temperature, the internal energy of the air in the room is, as long as the air pressure does not change, constant even if the room

---

[256] Choose $T_2 - T_1 = 1$ deg.

$$\begin{aligned} Q_1 &= -0.0013 \times 0.267 = -0.0003471 \text{ cal}, & (14.18)\\ Q_2 &= 0.0013 \times 0.267/1.421 = 0.0002443 \text{ cal} & (14.19)\\ &\Rightarrow Q_2 - Q_1 = 0.0001028 \text{ cal}. & (14.20)\end{aligned}$$

On the other hand, the work is obtained as $W = P\Delta V = 1033 \times 980 \times (1/274) = 3695$ erg $= 0.0003695$ J, so the work equivalent of heat is given by

$$0.0003695 \text{ J} = 0.0001028 \text{ cal} \;\Rightarrow \text{cal/J} = 3695/1028 = 3.59. \tag{14.21}$$

This should be 4.18, but the Mayer could not get very accurate source data.

is heated.[257]

Even if the room is perfectly thermally insulated, the energy loss still occurs with the air leaking from the room as a result of thermal expansion. If the room temperature is T, the number of moles $N(T)$ of air in the room is fixed by $PV = N(T)RT$, so the heat dQ needed for $T \to T + dT$ is given by

$$dQ = N(T)C_P dT = \frac{PVC_P}{RT} dT. \tag{14.23}$$

Therefore, the required energy to warm the room from T_1 to T_2 is obtained as

$$Q = \int_{T_1}^{T_2} dT\, \frac{PVC_P}{RT} = \frac{PVC_P}{R} \log \frac{T_2}{T_1} = C_P N_0 T_1 \log \frac{T_2}{T_1}, \tag{14.24}$$

where N_0 is the initial amount of air in the room.

To warm the N_0 mole air from T_1 to T_2, if the volume is constant, then the needed heat is $Q_V = N_0 C_V (T_2 - T_1)$; if the pressure is constant, then the needed heat is $Q_P = N_0 C_P (T_2 - T_1)$. What is the order of the magnitude of these needed heats?[258]

14.10 Reversible quasistatic and adiabatic process for ideal gas: Poisson's relation

For reversible quasistatic and adiabatic processes an ideal gas satisfies $PV^\gamma =$ constant. This is called *Poisson's relation*. Here, γ is the specific heat ratio as in **14.8**: $\gamma = C_P/C_V$.

For an ideal gas $dE = C_V dT$ under any condition (→**11.13**), so the P, V, T-relation in an adiabatic reversible and quasistatic process always satisfies

$$dE = -PdV = C_V dT \;\Rightarrow C_V dT + PdV = 0. \tag{14.25}$$

---

[257] R. Emden, Why do we have winter heating? Nature **141**, 908 (1938). Still, heating is costly despite (14.22). Where is all the money gone? The original discussion focused on the reason why the Earth does not heat up despite the Sun's radiation, and concluded that it is due to radiation emitted by the Earth.

[258] $Q_V < Q < Q_P$. The second inequality is physically obvious. The first inequality maybe understood as follows: Increase the temperature by dT under constant volume first. Then, to reduce the pressure to the original value, increase the volume. This process does work, so the temperature goes down. Therefore, to get the dT increase, we need a bit more energy. Thus, even if we take the reduction of the total amount of air due to leakage into account, we need more energy than the case of strictly constant volume.

Combining this with the equation of state $PV = RT$, we get

$$C_V dT + PdV = C_V d\left(\frac{PV}{R}\right) + PdV = \left(\frac{C_V}{R} + 1\right) PdV + \frac{C_V}{R} VdP. \tag{14.26}$$

Then, use Mayer's relation (14.13) and divide the result with PV:

$$C_P d\log V + C_V d\log P = 0 \;\Rightarrow\; d\log P + \gamma d\log V = 0. \tag{14.27}$$

Integrating this, we obtain Poisson's relation.

There should not be any entropy change before and after adiabatic, reversible and quasistatic processes. Confirm this (Answer[259]).

14.11 Temperature-altitude relation

When air ascends, we may approximate its thermal phenomenon by adiabatic, reversible and quasistatic expansion. Approximating air as an ideal gas, find how many degrees the air temperature goes down per 1 km ascending. This question is equivalent to the following:
At altitude z let the pressure, temperature and density, $P(z)$, $T(z)$, $\rho(z)$, respectively. The average molecular weight of air is M. Obtain $dT(z)/dz$.

The molar volume is $M/\rho(z)$, so the equation of state reads

$$P(z)M/\rho(z) = RT(z). \tag{14.29}$$

The force balance in the vertical direction for a horizontal disk of unit area with thickness dz (Fig. 14.2)tells us

$$P(z) + dP(z) + g\rho(z)dz = P(z). \tag{14.30}$$

Therefore,

$$\frac{dP(z)}{dz} = -\rho(z)g. \tag{14.31}$$

---

[259] The entropy of an ideal gas is given by its fundamental equation (11.26). Let us rewrite this with the aid of Mayer's relation (14.13) as:

$$S = S_0 + C_V\left[\log\frac{E}{E_0} + (\gamma - 1)\log\frac{V}{V_0}\right]. \tag{14.28}$$

Poisson's relation PV^γ with $P = RT/V$ gives $PV^\gamma \propto (T/V)V^\gamma = TV^{\gamma-1} =$ constant. For an ideal gas $E \propto T$ (→(11.23)), so we get $EV^{\gamma-1} =$ constant. Thus, (14.28) implies $S = S_0$.

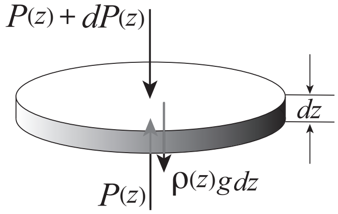

Figure 14.2: The force balance in the vertical direction for a horizontal disk of unit area with thickness dz

If we eliminate the density with the aid of the equation of state (14.29), we get

$$\frac{dP(z)}{dz} = -Mg\frac{P(z)}{RT(z)}. \tag{14.32}$$

We wish to have a differential equation for $T(z)$, so we use $P(T/P)^\gamma = P^{1-\gamma}T^\gamma =$ constant obtained from Poisson's relation PV^γ(→**14.10**) and the equation of state to write $P(z)$ in terms of $T(z)$. This relation gives $(1-\gamma)dP/P + \gamma dT/T = 0$, so (14.32) becomes

$$\frac{1}{P(z)}\frac{dP(z)}{dz} = -\frac{\gamma}{1-\gamma}\frac{1}{T(z)}\frac{dT(z)}{dz} = -Mg\frac{1}{RT(z)}. \tag{14.33}$$

That is,

$$\frac{dT(z)}{dz} = -\frac{Mg(\gamma-1)}{\gamma R}. \tag{14.34}$$

$M = 29$ g/mol, $\gamma = 1.41$, $R = 8.314 \times 10^7$ erg/K, and $g = 980$ cm/s^2 give about 10 K/km.

14.12 Reversible and quasistatic heat exchange

For simplicity, let us assume that the heat capacity of the system is constant C. The system has an initial temperature T. It is placed in thermal contact with a heat bath of temperature T_B ($> T$), and the temperature changes from T to $T + \delta T$. Let us also assume that the system is sufficiently small with good heat conductance and that δT is sufficiently small. Then, there is no irreversible process inside the system due to the inhomogeneity of the system temperature. The entropy change of the system is given by

$$\delta S_S = \int_T^{T+\delta T}\frac{CdT}{T} = C\log\frac{T+\delta T}{T} = C\left[\frac{\delta T}{T} - \frac{1}{2}\left(\frac{\delta T}{T}\right)^2 + O[\delta T^3]\right]. \tag{14.35}$$

The heat bath loses energy $C\delta T$ as heat, so its entropy change is given by

$$\delta S_B = -\frac{C\delta T}{T_B}, \tag{14.36}$$

since the heat bath temperature does not change. Therefore, the total entropy change of the system + heat bath reads

$$\delta S = \delta S_S + \delta S_B = C\left(\frac{1}{T} - \frac{1}{T_B}\right)\delta T - \frac{C}{2T^2}\delta T^2 + O[\delta T^3]. \tag{14.37}$$

Therefore, as long as $T \neq T_B$, however slowly the temperature is changed, still the term first order in δT remains, so the total entropy increases. Actually, if $\delta T > 0$, $T < T_B$ and if $\delta T < 0$, $T > T_B$ (Clausius' principle **8.3**), the first term of (14.37) is always positive unless $\delta T = 0$.

Consequently, only if $T = T_B$, if the change is slow (is quasistatic), entropy does not change.

By the way, isn't (14.37) a bit odd? The term δT^2 is negative, so as long as heat transfer is quasistatic, can we reduce the total entropy of system + heat bath adiabatically? This is ridiculous. Think (while hiding the footnote[260]) why we reached such a conclusion.

14.13 Stepwise heat exchange

14.12 suggests that if we reduce the temperature difference between the two systems in thermal contact, the increase of entropy is reduced. Suppose we wish to change

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[260] The reason for this ridiculousness is due to the system temperature changes from $T = T_B$ to $T_B \to T_B + \delta T$; irrespective of the sign of δT, the system in thermal contact with the heat bath of temperature T_B attains the temperature other than T_B, violating Clausius' principle. That is, (if we wish to have $\delta T > 0$ or $\delta T < 0$) the temperature should be $T_B - \delta T \to T_B$. For this change (14.35) becomes

$$\delta S_S = \int_{T_B-\delta T}^{T_B} \frac{CdT}{T} = -C\log\frac{T_B - \delta T}{T_B} = C\left[\frac{\delta T}{T_B} + \frac{1}{2}\left(\frac{\delta T}{T_B}\right)^2 + O[\delta T^3]\right]. \tag{14.38}$$

Therefore, the total entropy change is, when $T_B = T$,

$$\delta S = \delta S_S + \delta S_B = \frac{C}{2T_B^2}\delta T^2 + O[\delta T^3] > 0. \tag{14.39}$$

That is, just as the case of works (→**3.11**), if not performed quasistatically, even without temperature difference entropy increases.

the system temperature from T_1 to T_2 ($> T_1$). This suggestion implies that the entropy change due to the heat exchange by using a single heat bath of temperature T_2 should be larger than that due to the heat exchange in two steps, first $T_1 \to T_m$ by using a heat bath of an intermediate temperature T_m ($T_1 < T_m < T_2$), and then $T_m \to T_2$ by using a heat bath of temperature T_2. As long as $T_m \in (T_1, T_2)$ the total entropy change should be smaller. Is this true?

As **14.12** let us assume the system heat capacity C is constant and it is in thermal contact with a heat bath, but system + heat bath is isolated. First, the system temperature is initially T_1 and the heat bath is at temperature T_m. The total entropy change is given by

$$\Delta S + \Delta S_B = \int_{T_1}^{T_m} dT\,\frac{C}{T} - \frac{C(T_m - T_1)}{T_m} = C \log \frac{T_m}{T_1} - C\frac{T_m - T_1}{T_m}. \tag{14.40}$$

In the second step, the initial system temperature is T_m and the heat bath is at temperature T_2, so

$$\Delta S + \Delta S_B = C \log \frac{T_2}{T_m} - C\frac{T_2 - T_m}{T_2}. \tag{14.41}$$

Therefore, the total entropy change due to two steps is

$$\Delta S^{(2)} = C \log \frac{T_2}{T_1} + C\left[\left(\frac{T_1}{T_m} + \frac{T_m}{T_2}\right) - 2\right]. \tag{14.42}$$

The total entropy change due to one step is

$$\Delta S^{(1)} = C \log \frac{T_2}{T_1} + C\left[\left(\frac{T_1}{T_2}\right) - 1\right] = C \log \frac{T_2}{T_1} + C\left[\left(\frac{T_1}{T_2} + 1\right) - 2\right]. \tag{14.43}$$

Suppose A and B are positive numbers. Then the following function satisfies $f(A) = f(B)$ and strictly convex ($f''(T) = 2A/T^3 > 0$):

$$f(T) = \frac{A}{T} + \frac{T}{B}. \tag{14.44}$$

Therefore, $f(A) = f(B) > f(T)$ for any T between A and B ($\min f(T) = f(\sqrt{AB})$) implies $\Delta S^{(2)} < \Delta S^{(1)}$.

If we repeat this logic, as seen from (14.43), the term except for the log term would asymptotically vanish in the many step limit. That is, if we prepare various intermediate temperature heat baths, ultimately, we can change the system temperature quasistatically at our will. This 'ultimate situation' can be well approximated for fluid systems in a smart fashion (→**14.14**).

14.14 Reversible and quasistatic heat exchange for fluid systems: *rete mirabile*

For fluids, we can change its temperature reversibly; for example, by exchanging the temperatures between two fluids as shown in Fig. 14.3.

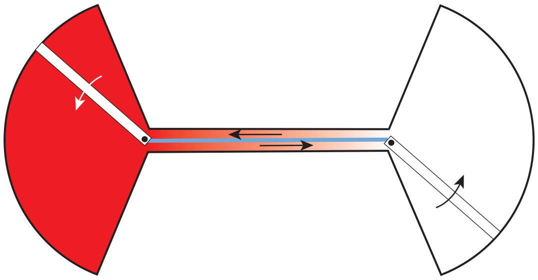

Figure 14.3: Two fan-shaped containers are connected by thin flat tubes in the middle. The containers have rotating adiabatic pistons and the two fluids do not mix. The thin tube is divided by a diathermal membrane (denoted by a blue line) to realize the so-called *countercurrent exchange*. The heat exchange becomes closer to quasistatic exchange if the tube becomes thinner. In this thin limit, the right and the left portions of the figure exchange matter, but there is no heat exchange at all, resulting reversible heat exchange between the two fluids.

A wiser method is to prepare numerous thin countercurrent exchange tubes and connect the two containers with these tubes as in Fig. 14.4.

Such an ingenious mechanism cannot be ignored by organisms. Such a device (organ) is called '*rete mirabile*' (pl. *retia mirabila*). For example, for water fowls *retia mirabila* in the legs and feet transfer heat from the outgoing (hot) blood in the arteries to the incoming (cold) blood in the veins. The same mechanism is utilized to maintain mammalian testes at low temperature (pampiniform plexus).[261] Not only heat but small ions and ATP exchange can use similar mechanisms (`https://en.wikipedia.org/wiki/Rete_mirabile`).

Lesson: Anything thermodynamics does not forbid may be realized.

14.15 Can we equate temperatures reversibly and quasistatically?

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[261] cf. B. R. Robinson, J. K. Netherton, R. A. Ogle, and M. A. Baker, Testicular heat stress, a historical perspective and two postulates for why male germ cells are heat sensitive, Biological Review **98**, 603 (2023).

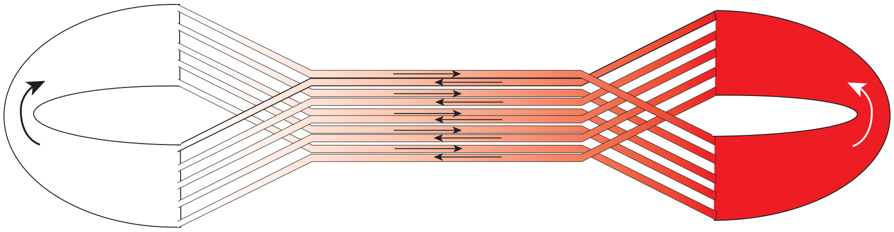

Figure 14.4: A schematic diagram of *rete mirabile*. If there is a mechanism to circulate fluid, fluids can be exchanged forever while separating the temperatures of the both parts.

Two blocks with identical heat capacities C are initially at temperature T_1 and T_2 ($> T_1$), respectively. If we bring them to thermal contact while isolating the whole system, they eventually reach a thermal equilibrium. The final temperature is $T_m = (T_1 + T_2)/2$ according to the first law. Therefore, the total entropy change is given by

$$\Delta S = \int_{T_1}^{T_m} \frac{CdT}{T} + \int_{T_2}^{T_m} \frac{CdT}{T} = C \log \frac{T_m}{T_1} + C \log \frac{T_m}{T_2} = 2C \log \frac{T_m}{\sqrt{T_1 T_2}}. \tag{14.45}$$

Needless to say, (since $-\log x$ is convex, due to Jensen's inequality **13.3**) $T_m = (T_1 + T_2)/2 > \sqrt{T_1 T_2}$, so $\Delta S > 0$; the process is neither quasistatic nor reversible.

If the final temperature is $\sqrt{T_1 T_2}$, there is no entropy change, so we may bring the two blocks to the same temperature reversibly and quasistatically. However, $T_1 + T_2 > 2\sqrt{T_1 T_2}$ implies that the total energy of the blocks must be reduced. Since the whole system is adiabatic, the internal energy must be reduced with a reversible work.

That is, between two heat sources whose temperatures are initially T_1 and T_2, respectively, we can operate a reversible engine (e.g., the Carnot engine **A.8**) (→**15.1**) until the temperature difference of the two sources disappears to realize the above situation. To check this explicitly may be a nice exercise of elementary thermodynamics.

15 Heat engine and heat pump

15.1 The efficiency of a reversible engine

A device that converts heat obtained from heat sources to work is called a *heat engine*. Thomson's principle **8.7** tells us that no engine works with only one heat source. Therefore, the metaprinciple **8.4** tells us that with two heat sources at different temperatures we can make a heat engine.

Suppose there are a high temperature heat source (→**8.3**) of temperature T_H and a low temperature heat source (→**8.3**) of temperature T_L ($< T_H$). Consider a heat engine that obtains heat Q_H from the high temperature heat source and Q_L from the low temperature heat source to deliver work $-W$ (> 0) (that is, the engine obtains work $W < 0$) during a single cycle. After one cycle the engine state returns to the original state, so the internal energy of the engine does not change:

$$W + Q_H + Q_L = 0. \tag{15.1}$$

To make a 'lossless' engine, according to the father and the son Carnot, the heat exchange between the engine and heat source must be performed quasistatically (→**A.6**-**A.8**), so the heat exchange must be done reversibly and quasistatically (i.e., isothermally →**14.12**). Due to the heat from the high-temperature heat source, the entropy of the engine changes by

$$\Delta S_H = \frac{Q_H}{T_H}. \tag{15.2}$$

Similarly, due to the heat from the low-temperature heat source, the entropy of the engine changes by

$$\Delta S_L = \frac{Q_L}{T_L}. \tag{15.3}$$

After the completion of a single cycle, the state of the engine returns to the original state, so there must not be any change in state quantities, in particular, in the engine entropy. Therefore,

$$0 = \Delta S_H + \Delta S_L = \frac{Q_H}{T_H} + \frac{Q_L}{T_L}. \tag{15.4}$$

An '*efficiency*' η is always considered as the ratio of 'gain'/'expenditure,' so for an engine the expenditure is the heat Q_H we supply from the high-temperature heat bath (a furnace), and the gain is the work $|W|$ engine produces. Notice that $W < 0$, since the energy balance is considered from the engine-centered point of view. Therefore, the efficiency of the engine is defined by

$$\eta = \frac{|W|}{Q_H} = -\frac{W}{Q_H}. \tag{15.5}$$

(15.1) implies

$$\eta = -W/Q_H = (Q_H + Q_L)/Q_H = 1 + Q_L/Q_H. \tag{15.6}$$

(15.4) gives

$$Q_L/Q_H = -T_L/T_H, \tag{15.7}$$

so that we get the efficiency of the reversible engine:

$$\eta = 1 - T_L/T_H. \tag{15.8}$$

15.2 Carnot's theorem: A reversible engine gives the efficiency upper bound

Consider a general engine functioning between the two heat sources as in **15.1**. What is its efficiency? That the efficiency of the reversible engine is the maximum is Carnot's theorem (→**A.8**, which is equivalent to other second laws →**8.13**). To demonstrate the theorem here we use Clausius' inequality **14.4**. If we remove the reversibility condition, (15.2) and (15.3) become

$$\Delta S_H \geq \frac{Q_H}{T_H}, \quad \Delta S_L \geq \frac{Q_L}{T_L}. \tag{15.9}$$

Except for this change, the remaining argument is the same as **15.1**. The overall change of entropy after one cycle is zero, so (15.4) is replaced by

$$0 = \Delta S_H + \Delta S_L \geq \frac{Q_H}{T_H} + \frac{Q_L}{T_L}. \tag{15.10}$$

Now, (15.7) is, since Q_H is positive, replaced by

$$Q_L/Q_H \leq -T_L/T_H. \tag{15.11}$$

This implies Carnot's theorem:

$$\eta = 1 + Q_L/Q_H \leq 1 - T_L/T_H. \tag{15.12}$$

15.3 Thermodynamic determination of absolute temperature scale

Absolute temperature is defined by (→(11.18))

$$\left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{Y}} = T. \tag{15.13}$$

Usually, the concept of absolute temperature is associated with Thomson, but do not forget that absolute temperature is essentially the temperature scale introduced by Carnot far before entropy.

Carnot (and Clapeyron) clearly recognized that the efficiency of the heat engine can be used as a thermometer. Especially, Carnot defined $\Theta(\theta)$ (later called the Carnot function) from the efficiency $\delta\eta$ of the Carnot engine functioning between two heat baths of empirical temperatures θ and $\theta - \delta\theta$:[262] ($\delta\theta > 0$)

$$\frac{\delta\eta}{\delta\theta} = \frac{1}{\Theta(\theta)}. \tag{15.14}$$

If absolute temperature T is a strictly increasing function of empirical temperature θ, (15.12) gives

$$\delta\eta = 1 - \frac{T(\theta - \delta\theta)}{T(\theta)} = \frac{T'(\theta)}{T(\theta)}\delta\theta. \tag{15.15}$$

That is,

$$\Theta(\theta) = 1 \bigg/ \frac{d\log T(\theta)}{d\theta} \tag{15.16}$$

It is convenient to use θ satisfying the equality $\Theta(\theta) = T(\theta)$. If this is required, (15.16) becomes $\Theta'(\theta) = 1$, so this is equivalent to demanding $\theta = \Theta = T$. This was emphasized much later by Thomson: this relation allows us to define temperature solely by the principle of thermodynamics independent of particular materials such as mercury or ethanol.

T already appeared in the equation of state of an ideal gas. Let us demonstrate this T is indeed the thermodynamically defined absolute temperature T defined by (15.13) (→**11.6**)

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[262] $\delta\eta = 1 - (T - \delta T)/T = \delta T/T = \delta \log T$.

15.4 T in the ideal gas equation of state is absolute temperature

Carnot conceived the following reversible engine that uses (1 mole of) an ideal gas as its working substance (Fig. 15.1):
(i) The engine does work through expansion while absorbing heat from the high temperature heat source (at T_H) (A→B in Fig. 15.1).
(ii) Then, it continues to expand while doing work and cools from T_H to T_L (B→C). Notice that this portion was Watt's novelty in his engine appreciated highly by Carnot as noted in **A.4**.
(iii) Next, the engine volume isothermally shrinks (i.e., the engine is done some positive work) while discarding heat to the low temperature heat source at T_L (C→D).
(iv) Finally, the system is compressed adiabatically (the engine is done some positive work as well) and its temperature goes up from T_L to the original T_H (D→A).

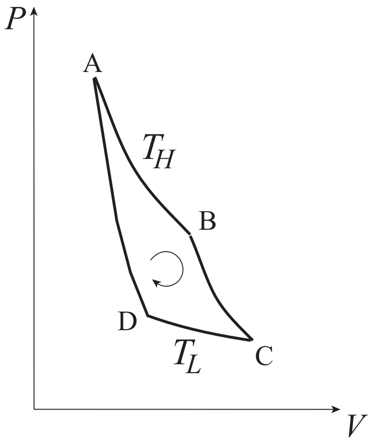

Figure 15.1: The Carnot cycle: AB and CD are quasistatic isothermal processes, and BC and DA are quasistatic adiabatic processes. The working substance is an ideal gas, so during the isothermal process its internal energy is constant. This implies that during isothermal processes the work the system does (or is done to the system) and the heat it absorbs (or it discards) must be identical.

The work added to the system (= the engine) is given by (note that $W < 0$, since the engine gives us work $|W|$)

$$W = -\oint_{\mathrm{ABCDA}} PdV \tag{15.17}$$

That is, the work $|W|$ done by the engine per cycle is given by the area enclosed by the figure in Fig. 15.1.

During the isothermal process A→B the engine does work, but the internal energy of the ideal gas does not change without temperature change (→(11.23)). Therefore, this work must be supported by the heat Q_H absorbed from the heat bath at temperature T_H. Therefore,

$$Q_H = \int_{\mathrm{A}\to\mathrm{B}} PdV = \int_{\mathrm{A}\to\mathrm{B}} \frac{RT_H}{V} dV = RT_H \log \frac{V_B}{V_A} > 0. \tag{15.18}$$

According to the similar logic, the heat $|Q_L|$ released to the low temperature heat bath (the system absorbs heat Q_L (< 0)) during the isothermal process C→D must be the same as the work done to the system:

$$|Q_L| = -\int_{\mathrm{C}\to\mathrm{D}} PdV = \int_{\mathrm{C}\to\mathrm{D}} \frac{RT_L}{V} dV = RT_L \log \frac{V_C}{V_D}. \tag{15.19}$$

To relate these two heats we need the volume relations during the reversible adiabatic process. From Poisson's relation (→**14.10**) PV^γ = constant, so we see $TV^{\gamma-1}$ = constant. Therefore, we have $T_H V_{\mathrm{A}}^{\gamma-1} = T_L V_{\mathrm{D}}^{\gamma-1}$ and $T_H V_{\mathrm{B}}^{\gamma-1} = T_L V_{\mathrm{C}}^{\gamma-1}$. Thus, $T_H/T_L = V_{\mathrm{D}}^{\gamma-1}/V_{\mathrm{A}}^{\gamma-1} = V_{\mathrm{C}}^{\gamma-1}/V_{\mathrm{B}}^{\gamma-1}$, that is, $V_{\mathrm{B}}/V_{\mathrm{A}} = V_{\mathrm{C}}/V_{\mathrm{D}}$ holds, since $\gamma > 1$. Using this relation in (15.18) and (15.19), we obtain (15.4). The remaining argument is just as in **15.1** and we obtain (15.8). Hence, T in the ideal gas equation of state is the thermodynamic absolute temperature.

15.5 The efficiency of reversible engine with more than two heat sources

For a reversible engine working with heat Q_i supplied by the i-th heat bath of temperature T_i there is no entropy change for a cycle, so the general Clausius' equality (→**14.5**) holds:

$$\sum_i \frac{Q_i}{T_i} = 0. \tag{15.20}$$

To be clear, if $Q_i > 0$ (resp., $Q_i < 0$), then Q_i will be marked with + (resp., with −) as Q_i^+ (resp., Q_i^-). Then, (15.20) reads

$$\sum_{+i} \frac{Q_i^+}{T_i} + \sum_{-i} \frac{Q_i^-}{T_i} = 0. \tag{15.21}$$

Now, let us replace the temperatures of the heat source supplying + heat with the highest temperature $T_{\max}$ among the temperatures of the heat baths. We get

$$\sum_{+i} \frac{Q_i^+}{T_i} \geq \frac{\sum_{+i} Q_i^+}{T_{\max}}, \tag{15.22}$$

Similarly, let us replace the temperatures of the heat source supplying $-$ heat with the lowest temperature $T_{\rm min}$. We get (since $Q_i^- < 0$)

$$\sum_{-i} \frac{Q_i^-}{T_i} \geq \frac{\sum_{-i} Q_i^-}{T_{\rm min}}. \tag{15.23}$$

Adding these two inequalities and write $Q^{\pm} = \sum Q_i^{\pm}$. (15.20) implies

$$\frac{Q^+}{T_{\rm max}} + \frac{Q^-}{T_{\rm min}} \leq 0. \tag{15.24}$$

Notice that this inequality has the same structure as (15.10).

The conservation of energy implies $W + Q^+ + Q^- = 0$. The efficiency of the engine η should be defined as work/total expenditure, so its calculation becomes exactly the same as the calculation of the efficiency of an engine working with two heat sources:

$$\eta = \frac{W}{Q^+} \leq 1 - \frac{T_{\rm min}}{T_{\rm max}}. \tag{15.25}$$

"More general" Carnot's theorem[263] The proof of Carnot's theorem in **15.2** requires, strictly speaking, equilibration of the engine after every cycle. To remove (or reduce the effect of) this restriction, we may use n ($\gg 1$) cycles as a single cycle. Furthermore, during this long operation of an engine, the source temperatures need not be constant. Note that this variable source temperature problem can be cast as the many heat source problem just discussed (→**15.5**), so the available max and min temperatures are written T_H and T_L, respectively, and the overall efficiency is given by (15.25).

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[263] This is emphasized by H Tasaki in an Appendix of his *Thermodynamics*.

16 Equilibria between two systems

16.1 Equilibrium condition between two systems

Let us prepare two systems I and II whose equilibrium states may be expressed in terms of an identical set of thermodynamic coordinates $(E, \boldsymbol{Y})$. Assume that these two systems as a whole are isolated and in contact with each other through various walls (= various boundary conditions). Allow the exchange of an operational coordinate between I and II. Then, the entropy of I + II cannot be less than the sum of the original entropies before coming into contact according to the principle of increasing entropy (→**12.3**):

$$S_{\mathrm{I+II}} \geq S_{\mathrm{I}} + S_{\mathrm{II}}. \tag{16.1}$$

In particular, the entropy maximization principle **12.4** implies that after reaching the new equilibrium state $S_{\mathrm{I+II}}$ must be maximized for the exchanged coordinate. This is the most general equilibrium condition.

$-S_{\mathrm{I+II}}$ is (substantially →**13.1** footnote) convex, so its minimum is unique and global. Thus, the local maximum of $S_{\mathrm{I+II}}$ is global, and the max value is unique.

However, the max value may not be given by the extremal value of $S_{\mathrm{I+II}}$. Therefore, for example, if an operational coordinate Y is exchanged between I and II, and if Gibbs' relation is

$$dS = \frac{1}{T}dE - \frac{y_1}{T}dY_1 - \cdots - \frac{y}{T}dY - \cdots, \tag{16.2}$$

the equilibrium condition need not be obtained from the extremal principle:[264]

$$\frac{\partial}{\partial Y_{\mathrm{I}}}S_{\mathrm{I}} - \frac{\partial}{\partial Y_{\mathrm{II}}}S_{\mathrm{II}} = 0 \tag{16.3}$$

or the identity $y_{\mathrm{I}}/T_{\mathrm{I}} = y_{\mathrm{II}}/T_{\mathrm{II}}$. For each thermodynamic coordinate, we must check whether (16.3) is admissible.

16.2 Equilibrium due to thermal contact

Let us consider the case where only E can be exchanged among the thermodynamic

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[264] As noted already, we allow chemical reactions to occur.

coordinates $(E, \boldsymbol{Y})$.[265] This implies that only heat exchange can occur between I and II (or, I and II are in thermal contact →**7.12**). (16.1) becomes

$$S_{\mathrm{I+II}}(E) \geq S_{\mathrm{I}}(E_{\mathrm{I}}) + S_{\mathrm{II}}(E - E_{\mathrm{I}}), \tag{16.4}$$

and the E_{I} that maximizes the right-hand side gives the equilibrium condition. However, whether the condition is an extremal condition or not is not automatically clear.

Temperature is defined so that (1) the temperatures of two systems in thermal contact are equal if and only if they are in thermal equilibrium (→**7.12**), and that (2) the 'high' or 'low' of temperature is defined consistently with the direction of heat flow (consistent with Clausius' principle **8.3**) (→**11.6**). Therefore, in particular, thermal equilibrium is equivalent to temperature equilibrium (equality), so (→**11.11**)

$$\left(\frac{\partial S_{\mathrm{I}}(E_{\mathrm{I}})}{\partial E_{\mathrm{I}}}\right)_{\boldsymbol{Y}_{\mathrm{I}}} + \left(\frac{\partial S_{\mathrm{II}}(E - E_{\mathrm{I}})}{\partial E_{\mathrm{I}}}\right)_{\boldsymbol{Y}_{\mathrm{II}}} = \frac{1}{T_{\mathrm{I}}} - \frac{1}{T_{\mathrm{II}}} \tag{16.5}$$

must vanish in thermal equilibrium. That is, the thermal equilibrium condition is an extremal condition.

Note that the equality of temperature is not the consequence of the entropy maximization principle (→**12.4**). The logic is the other way around: the fact that thermal equilibrium is the temperature equality (and the concavity of entropy) implies that the entropy is extremized in thermal equilibrium. Thus, we may say that the thermal equilibrium condition may be written as a principle for entropy, but it is not derived from the requirement for entropy.

16.3 Infimal convolution

When a certain thermodynamic coordinate is exchanged between two systems, the entropy after reaching equilibrium between the two systems is determined by the principle of maximizing entropy (→**12.4**). The entropy of the compound system thus formed is again a concave function, if coordinates are additive (not merely partition additive →**2.13**).

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[265] Needless to say, the chemical equilibria shift, so the chemical composition of the system cannot be fixed, generally speaking. Therefore, with the conventional choice of the chemical coordinates as in most text books, changing E while fixing all the thermodynamic coordinates is generally impossible. Thus, for example in the chemical thermodynamics book by Kirkwood and Oppenheim, no chemical reaction is permitted when Gibbs' relation is discussed. Furthermore, reactions are halted when partial derivatives with respect to the ordinary thermodynamic coordinates are computed to avoid mathematical difficulties of keeping chemical composition variables constant. After entropy maximization with frozen reactions, do they allow reactions to proceed? Then, the states of I and II change, so the equilibrium temperature would also change. Thus, do they discuss iterative way to determine the equilibrium condition?

The general theorem behind this fact is the theorem of *infimal convolution*. Let f and g be convex functions: $\mathbb{R}^n \to \mathbb{R}$. Then, the following construction

$$h(x) = \inf_{x=x_1+x_2}[f(x_1)+g(x_2)] \equiv (f\,\Box\,g)(x) \tag{16.6}$$

is called *infimal convolution*. The resultant function is also convex.

[Demonstration] Let us demonstrate Jensen's inequality (→**13.3**) directly:

$$\begin{aligned}
\lambda h(x) + (1-\lambda)h(x') &= \lambda \inf_{x=x_1+x_2}[f(x_1)+g(x_2)] + (1-\lambda)\inf_{x'=x'_1+x'_2}[f(x'_1)+g(x'_2)] \\
&= \inf_{x=x_1+x_2,x'=x'_1+x'_2}\{\lambda[f(x_1)+g(x_2)]+(1-\lambda)[f(x'_1)+g(x'_2)]\} \\
&= \inf_{x=x_1+x_2,x'=x'_1+x'_2}\{[\lambda f(x_1)+(1-\lambda)f(x'_1)]+[\lambda g(x_2)+(1-\lambda)g(x'_2)]\} \\
&\geq \inf_{x=x_1+x_2,x'=x'_1+x'_2}[f(\lambda x_1+(1-\lambda)x'_1)+g(\lambda x_2+(1-\lambda)x'_2)] \qquad (16.7) \\
&\geq \inf_{\lambda x+(1-\lambda)x'=\lambda(x_1+x_2)+(1-\lambda)(x'_1+x'_2)}[f(\lambda x_1+(1-\lambda)x'_1)+g(\lambda x_2+(1-\lambda)x'_2)] \qquad (16.8) \\
&= h(\lambda x+(1-\lambda)x'). \qquad (16.9)
\end{aligned}$$

Here, in (16.8) note that fixing x and x' independently is conditionally more constrained than fixing $\lambda x + (1-\lambda)x'$.

16.4 Equilibrium states attained through work coordinate exchanges

The equilibrium of the resultant compound system realized through exchange of work coordinates between systems I and II has the entropy obtained by infimal convolution (→**16.3**, because $-S$ is convex). For example (→**16.1**) (here, only one work coordinate X and internal energy E are explicitly written; other operational coordinates are all fixed)

$$S(E,X) = \sup_{X=X_{\mathrm{I}}+X_{\mathrm{II}}}[S_{\mathrm{I}}(E_{\mathrm{I}},X_{\mathrm{I}})+S_{\mathrm{II}}(E_{\mathrm{II}},X_{\mathrm{II}})] \tag{16.10}$$

is automatically concave. However, the condition sup need not be realized by an extremal condition. As noted already in **16.1**, this depends on the domain of the entropy function, so there is no general theory as we will see in **16.6**.

If the max condition can be obtained from the extremal condition, the equilibrium condition reads

$$\left(\frac{\partial S_{\mathrm{I}}}{\partial X_{\mathrm{I}}}\right)_{X^c{}_{\mathrm{I}}} + \left(\frac{\partial S_{\mathrm{II}}}{\partial X_{\mathrm{II}}}\right)_{X^c{}_{\mathrm{II}}} = \frac{x_{\mathrm{I}}}{T_{\mathrm{I}}} - \frac{x_{\mathrm{II}}}{T_{\mathrm{II}}}, \tag{16.11}$$

where X^c means to remove X from the totality of the operational coordinates $\boldsymbol{Y}$.

16.5 Equilibrium states attained through contacts allowing chemical exchanges

Let us keep E and the operational coordinates $\boldsymbol{Y}$ other than the mole number N of one chemical, and exchange only this chemical substance between two systems I and II to obtain a new equilibrium. Assume the two systems as a whole is materially closed for simplicity:

$$S(E, N, \boldsymbol{Y} \setminus N) = \sup_{N_{\mathrm{I}}+N_{\mathrm{II}}=N} [S_{\mathrm{I}}(E, N_{\mathrm{I}}, \boldsymbol{Y}_{\mathrm{I}} \setminus N_{\mathrm{I}}) + S_{\mathrm{II}}(E, N_{\mathrm{II}}, \boldsymbol{Y}_{\mathrm{II}} \setminus N_{\mathrm{II}})]. \tag{16.12}$$

Here, N and $\boldsymbol{Y}$ on the left-hand side are given by the sum of $N_{\mathrm{I}}, N_{\mathrm{II}}$ and $\boldsymbol{Y}_{\mathrm{I}}, \boldsymbol{Y}_{\mathrm{II}}$, respectively. The actual material exchange process may be imagined as illustrated here (Fig. 16.1):

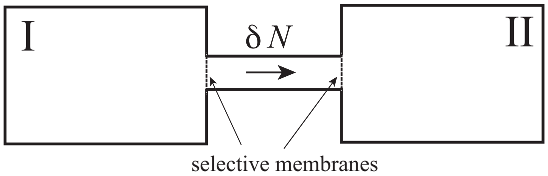

Figure 16.1: The two systems are connected via selective membranes allowing only the designated chemical to go through. The central connecting portion is not needed, but is here to clearly show that only the target component is exchanged.

To begin with, let us recall what happens if a chemical is introduced by a small amount δN into the system. Note that the reactions do not contribute any energy change near equilibrium. That is, the case with reactions is exactly the same as the case without reactions, although the actual changes of the chemical components may be different.

Now, let us consider the exchange of a chemical between two systems I and II as illustrated in Fig. 16.1. It is clear at each end of the connecting 'pipe', the situation is exactly as we considered above. Therefore, the chemical potential of this compound must agree between I and II. Thus,

$$\left(\frac{\partial S_{\mathrm{I}}}{\partial N_{i\mathrm{I}}}\right)_{E_{\mathrm{I}}, \boldsymbol{X}_{\mathrm{I}}, \boldsymbol{N}_{\mathrm{I}}^{i}} + \left(\frac{\partial S_{\mathrm{II}}(N_i - N_{i\mathrm{I}})}{\partial N_{i\mathrm{I}}}\right)_{E_{\mathrm{II}}, \boldsymbol{X}_{\mathrm{II}}, \boldsymbol{N}_{\mathrm{II}}^{i}} = \frac{\mu_{i\mathrm{I}}}{T_{\mathrm{I}}} - \frac{\mu_{i\mathrm{II}}}{T_{\mathrm{II}}}, \tag{16.13}$$

where ^{i} implies to remove N_i.

16.6 Pressure equilibrium

If two systems interact through a wall that allows exchange of volume (that is, through a movable piston) only, and if there is no restriction for the range of the wall (except for the nonnegativity of the volumes), (16.3) becomes

$$\left(\frac{\partial S_{\mathrm{I}}}{\partial V_{\mathrm{I}}}\right)_{\boldsymbol{X}_{\mathrm{I}}\backslash V_{\mathrm{I}},\boldsymbol{N}_{\mathrm{I}}} = \left(\frac{\partial S_{\mathrm{II}}}{\partial V_{\mathrm{II}}}\right)_{\boldsymbol{X}_{\mathrm{II}}\backslash V_{\mathrm{II}},\boldsymbol{N}_{\mathrm{II}}} \tag{16.14}$$

This implies

$$\frac{P_{\mathrm{II}}}{T_{\mathrm{I}}} = \frac{P_{\mathrm{II}}}{T_{\mathrm{II}}}. \tag{16.15}$$

If the wall is not adiabatic, this means that the pressures must agree.

However, in this case it is easy to restrict the range of the volume; we have only to place stoppers for the piston (Fig. 16.2). Needless to say, the agreement of P/T does not hold. Still, the total entropy is maximized under the presence of stoppers.[266,267] The value is not extremum, but is on the boundary of the domain of the volume variable.

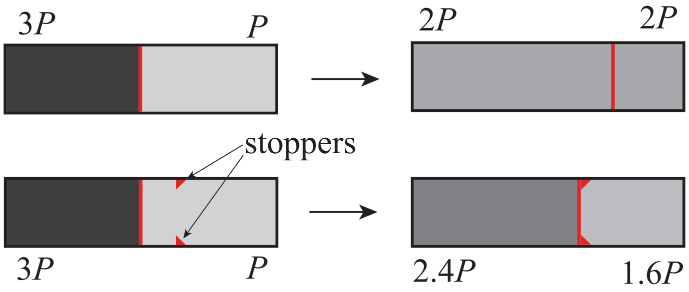

Figure 16.2: Pressure equilibria of ideal gases with and without stoppers; the red wall is movable and diathermal. In both cases, the entropy is maximized under the conditions.

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[266] Even in this case we can directly apply infimal convolution (→**13.2**). The reader might be worried about the range of the variables, but there is no difficulty, if we redefine our convex function f whose domain is C as a convex function f whose domain has no boundary but $f = +\infty$ outside C (the standard choice in convex analysis as noted in the footnote of **13.1**).

[267] Complication due to dry friction: If there is dry friction between the piston and the cylinder, it is hard to determine the final position of the piston. Therefore, the final equilibrium states are not unique. In this case, can we control the final state precisely by fine-tuning the initial condition? Since the mechanism of dry friction is rather microscopic, the author is pessimistic.

It seems to be possible to 'impose stoppers' to work coordinates. This is quite different from the heat exchange.[268]

16.7 Adiabatic piston

Consider an adiabatic box with an adiabatic piston as illustrated in Fig. 16.3.

Figure 16.3: An adiabatic box equipped with an adiabatic piston (blue)

Suppose, for example, System II is initially at a higher pressure than System I. Releasing the piston, we wait for a long time. What is the eventually reached equilibrium state?

To determine the states of the system, we must determine all the thermodynamic coordinates of both systems. If both the boxes are filled with gases, we must determine the following four extensive variables: $E_{\mathrm{I}}, E_{\mathrm{II}}, V_{\mathrm{I}}$, and V_{II}. The sum of internal energies and volumes are conserved. Furthermore, the pressures must be identical. Thus, we have three equalities. With one more equation, the states are completely determined. The relation may be a relation holding for System I only (for example, the gas in I undergoes a polytrope change[269]).

If we perform the experiment reversibly and quasistatically, then the total entropy must also be preserved, so the final equilibrium state must be unique. For example for an ideal gas, Poisson's relation uniquely determine the final temperatures and the piston position.

What happens, then, if the process is not quasistatic? Since the process is not quasistatic, dissipations of kinetic energy must occur in the systems. The details

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[268] Generally speaking, it seems very hard to invent stoppers for extensive quantities whose exchanges are due to accumulations of 'microscopic exchanges.' That is, to invent (macroscopic) stoppers for materials coordinates seems almost impossible.

[269] A polytropic process is a process for which PV^n is constant for some $n > 0$. This is used to approximately describe various actual processes. The final state depends on n; This implies that the final equilibrium state depends sensitively to the actual process.

of the process, such as friction between the piston and the wall, determine how the kinetic energy is distributed between I and II, making the resultant equilibrium state an open set in $\mathcal{E}$.

For example, if there is no friction at all between the piston and the walls, the piston starts to oscillate, and irreversible expansions and compressions of the gases occur. Thus, the kinetic energy is distributed to I and II through heating of the gases. In general, however, there is a friction between the piston and the wall, so heat is also generated at the piston-wall contact as well. This depends on the details of the piston and the wall, and we must also consider how the generated heat is distributed between I and II. Thus, even macroscopically many different outcomes can occur, so the resultant equilibrium state cannot be unique.[270]

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[270] We can make examples like the adiabatic piston for many other situations. For example,. consider an adiabatic wall allowing the exchange of chemical B. Assume for simplicity the volume do not change. If we can determine E and N_{B} the states are determined. There are four quantities we must determine for the two systems. The total energy and the total amount of B are fixed without chemical reaction. Furthermore, the chemical potential of B must agree. We have three relations. We must worry about the method to transfer B between the two systems; there can be numerous different ways.

17 Mixing entropy

17.1 Review: Open systems and closed systems

Up to this point for simple and compound systems, the usual electromagnetic/mechanical works and the chemical works are treated basically without much distinction. However, we already know chemical coordinates are not as simple as the usual work coordinates (esp.,see Section 5).

A system is said to be *closed*, if it does not exchange any material with its environment. In conventional thermodynamics, closed systems are first considered, and then the so-called mass action Z ($= \zeta$ in **4.13**) due to materials exchange is taken into account. The conservation law of energy (the so-called first law →**7.14**) is extended to include the Z term:

$$\Delta E = Q + W + Z. \tag{17.1}$$

Based on this equation the thermodynamics of open systems is developed traditionally. That is, once the 'first law' is generalized as (17.1), the thermodynamics of open systems is constructed without any new empirical facts or principles.

However, since thermodynamics is a phenomenology, clear supporting empirical statements are desirable that the general theory of open systems based on (17.1) can be constructed even if chemical reactions occur.

This book attempts to minimize the deviation from conventional textbooks while correcting them. Still, it is worth noting that chemistry is not straightforward. For the convenience of those who may have avoided chemistry until this point, an explanation of how to choose chemical coordinates and their controllability will be repeated.

17.2 Amount of materials as thermodynamic coordinates

The conservation of energy may be assumed to hold as (17.1), but what about the second law? Does it remain intact even with chemical coordinates? Since thermodynamics began with the study of the relationship between heat and work, the second law more or less explicitly mentions work and work coordinates, but chemical coordinates and chemical energy are not mentioned until open systems are considered.

The problem we must consider is whether we may handle the work coordinates and the chemical coordinates as the quantities of the same nature. Heat and work are, even if energetically their amounts are the same, thermodynamically fundamentally different quantities (→**A.10**, **8.3**). How about chemical work (mass action) thermodynamically?

To assert that work coordinates and chemical coordinates are the quantities of the same nature, we must verify that no constraints as stated by the second law is imposed on the mutual conversion of work and chemical coordinates [or, if we adopt Clausius' expression (→**A.11**), without any compensation].

17.3 What is the meaning of non-existence of restrictions due to the second law?

Let us review the relationship between heat and work: According to Mayer and Joule, we can convert work W to heat Q at temperature T (without any other trace) (→**7.14**). Then, we cannot restore W from the resultant heat Q to restore the original 'world' state as shown by Carnot [We must consume a part of Q for compensation (→**A.11**; Fig. 17.1 I)].[271]

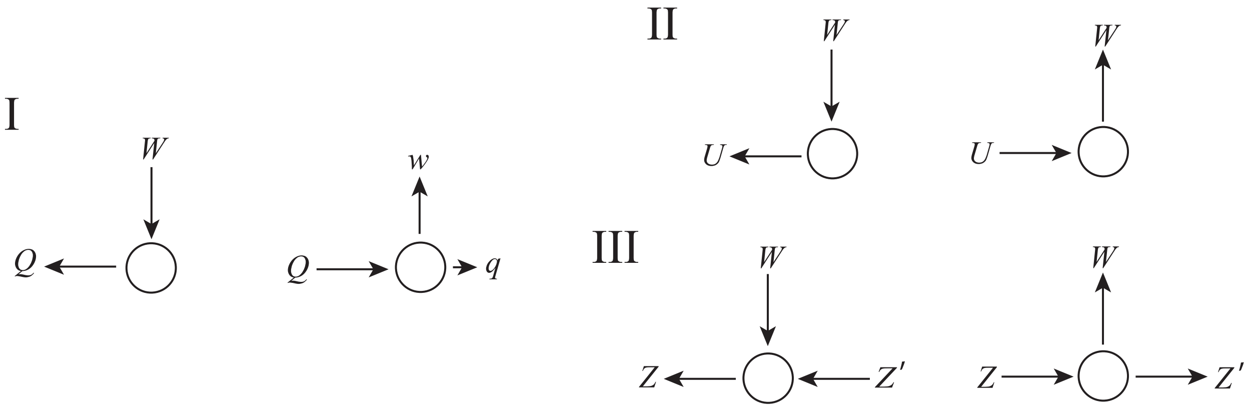

Figure 17.1: Possible constraints due to the second principle: Q, q ($< Q$) heats; W, w ($< W$): works; U: potential energy; Z, Z': chemicals (the so-called mass actions). For all cases the state of the device denoted by a circle must return to the original state after the process.

In contrast, there is no such restriction on the relationship between mechanical potential energy and work (without any friction and all the processes must be quasistatic; Fig. 17.1 II). If work W is converted to the potential energy U, it is possible to convert U to work W exactly without leaving any trace other than, e.g., lowering

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[271] Needless to say, we can convert heat 100% to work utilizing an isothermal expansion process of a gas, but in this case the gas changes its volume, so it is not without trace as illustrated in **8.7**.

the weight; this is the meaning of 'without the restriction imposed by the second law [i.e., no compensation in Clausius' sense (→**A.11**) is required].

Needless to say, the U-W relation is an empirical fact established in macroscopic mechanics and/or electromagnetism.

How about chemical energy Z and work W? Is there any restriction imposed by the second law or something similar? To convert chemical energy carried by chemical compounds, usually, material exchange is inevitable, although all the reactions may happen in a closed system. Here, the circles in Fig. 17.1 denote 'converters' (an engine, a motor, etc.), In the conversion between W and Z the device may be a (reversible) electric cell, so W may be electric potential energy. 'Chemical fuel' with the energy Z is introduced and then 'chemical exhaust' Z' is discarded ($W = Z - Z'$).

We must establish the W-Z relation empirically as well: switching the exhaust Z' and the fuel Z, 'W' can 'restore' the fuel perfectly. To study this what kind of experiments should we perform? Perhaps, the most effective experiments are electrochemical experiments, using electric cells. The importance of electrochemistry is not only because of recent practical applications, but also from a fundamental science point of view.

In essence, the reversible relation between electric cell reactions and electrolytic reactions demonstrates the equivalence of chemical work and ordinary work.[272]

In summary, it is empirically justified to extend Thomson's principle **8.7** and Planck's principle **8.5** to versions that include not only ordinary works but also generalized works, such as chemical works. Work coordinates and chemical coordinates (more precisely, materials coordinates) can be considered thermodynamic coordinates (and are collectively referred to as operational coordinates). Our second laws have already been extended to cover chemical reactions[273] (Section 8).

17.4 Why the conventional chemical thermodynamics is not logical

As noted in **17.2**, the conventional approach is to complete the thermodynamics without any chemical reaction and then graft chemistry to it. For this approach to be admissible, the basic principles of thermodynamics, especially the second law, must also apply to chemical reactions. Unfortunately, however, Thomson's principle and Planck's principle must be augmented to this end. If the work-chemical work

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[272] As already seen in **A.16** the establishment of the first law and this observation was intertwined.

[273] However, as emphasized repeatedly, do not forget that the changes of chemical coordinates must be handled with care.

equivalence (→**17.3**) is explicitly stated, we do not need to revise Thomson's principle. However, for Planck's principle (→**8.5**), the fundamental difference between the work coordinates and chemical composition variables (→**4.9**) must be taken into account as in **8.5**.

Clausius' principle (→**8.3**) remains unchanged even with chemical reactions. This is because the principle retains the same form in any restricted world (say, the world where chemical reactions are forbidden). Thus, even if Planck's principle can derive Clausius' principle, this proof is in the world where a particular version of Planck's principle holds, e.g., in a world where chemical reactions are prohibited.

The construction of the foliations of the thermodynamic space requires a principle equivalent to Planck's principle. Therefore, to construct entropy that can cover chemical reactions, it must be based on Planck's principle revised to include chemical reactions explicitly (→**8.5**).

If chemical changes are prevented, then for a given system the internal energy and the work coordinates cannot generally be altered in the world where chemical reactions occurs.

Therefore, to incorporate chemical reactions into a thermodynamic system, the entropy of this thermodynamic system must be constructed in the world where chemical reactions are permitted.

Thus, the 'rootstock' for chemical thermodynamics must be specially prepared to graft chemistry; chemical reactions should be incorporated into thermodynamics from the beginning. See **4.16** about the problems of the conventional chemical thermodynamics.

17.5 Selectively permeable membrane and mass action

There are numerous distinct materials (chemicals). We must assume that we can distinguish them, since they are considered distinct. While distinguishing distinct chemicals is the job of chemistry, in thermodynamics, we must assume that we can (at least in principle) specify the chemicals that may be exchanged between the system and its environment. This assumption is equivalent to the one that we can specify the properties of the walls enclosing the system accordingly.

The idealized device that enables this procedure is the *selectively permeable membrane* (henceforth, *selective membrane* to be short), which allows only a specified set of chemicals to be exchanged across it. In principle, it can distinguish stereoisomers and isotope-replaced compounds.[274] The amount of a compound may be measured in any manner, but it is convenient to use mole numbers to describe chemical reactions. Therefore, unless stated otherwise, mole numbers will be used to describe the amount of a compound. If the amount of a chemical is changed by dN adiabatically and quasistatically, the system energy change will be written as[275]

$$dZ = \mu dN. \tag{17.2}$$

Here, N is an extensive quantity. Generally, there are many different compounds;

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[274] The selectively permeable membrane is equivalent to the commonly used 'semipermeable membrane' in elementary thermodynamics. Some authors try to avoid the use of such a device, arguing that it "cannot exist" in reality. However, here, our basic idea is that such objections to semipermeable membranes arise due to misunderstanding of the concept of the selective membrane (→**4.15**).

The selective membrane is a black box that represents high precision separating processes. Selective membranes appear everywhere in organisms with high precision (for isotope replacement the precision is limited but still not non-selective). They may not be passive, so to use them in thermodynamics is often claimed to be illegitimate. However, since equilibrium thermodynamics does not impose any limit on the conversion of work to chemical work, even active separation processes can be realized quasistatically, so where there is separability (= distinguishability) of compounds, we may assume that we can separate them quasistatically and reversibly. Therefore, wherever compounds are separable (= distinguishable), we can separate them quasistatically and reversibly, and the process may be summarized as a selective membrane. For example, pure substance A can be separated by distillation (e.g., multi-stage distillation) from a mixture. The needed phase transitions can be reversibly and quasistatically realized. We can add pure A to another system reversibly and quasistatically as well. Describing such processes in terms of selective membranes as black boxes should be perfectly consistent with thermodynamics (recall, e.g., adiabatic walls). In the case of biomembranes, a selective transport of a particular compound across it could be accompanied by the consumption of ATP or by the countercurrents of other compounds, but even active transport can be described in terms of (chemical) works and should be possible to realize as a reversible and quasistatic process; it is a matter of ingenuity since thermodynamics does not forbid it.

Thus, in short, any distinguishable compounds maybe reversibly and quasistatically separable. This should be a chemical principle (→**4.3** (I)), and its materialization is the selective membrane (like an ohmic resistor in the circuit theory).

There is a famous quiz: can we tell chemicals A and B are identical or different compounds by measuring their mixing entropy? As is well known, this is impossible since the measurement of the mixing entropy requires a cycle recovering pure A and B from the mixture. Conversely, if we know A and B are different, we can in principle separate them quasistatically, and their mixing entropy may be measured.

If we accept the principle used here, we may assume that a selective membrane exists for any pure substance.

[275] Here, dZ is, as dQ, a symbol for a 1-form and does not imply the differential of Z.

they are distinguished by suffixes as

$$dZ = \sum_i \mu_i dN_i. \tag{17.3}$$

μ_i is called the *chemical potential* of chemical i. dN_i is the amount of chemical i added by the experimenter to the system (the increment of the materials coordinate for chemical i as discussed in **4.13**).

Remark: Probably, it is no more necessary by now to repeat, but the actual amount of chemical i in the system may not change by dN_i due to chemical reactions.

17.6 Thermodynamic space for open systems

To describe thermodynamics we need the internal energy and operational coordinates consisting of work coordinates and materials coordinates (as chemical coordinates). As stated in **17.2** thermodynamically work and chemical coordinates are 'equivalent' with respect to the second law.

Thus, we write Gibbs' relation **11.8** as

$$dE = TdS + \sum_i x_i dX_i + \sum_i \mu_i dN_i. \tag{17.4}$$

Or, if entropy is placed at the center of the organization of thermodynamics,

$$dS = \frac{1}{T}dE - \sum_i \frac{x_i}{T}dX_i - \sum_i \frac{\mu_i}{T}dN_i. \tag{17.5}$$

17.7 Chemical potential

A basic (albeit not practical) operational method to determine the chemical potential μ_i of chemical i is illustrated in (Fig. 17.2).

A small cylinder containing only chemical i is attached to the system. A hard selectively permeable membrane that allows only i to pass is placed between the cylinder and the system. The work required for this process can determine μ_i.[276]

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[276] Needless to say, the process must be reversible and quasistatic. However, whether such a process is realizable or not cannot be decided by speculation. For example, one must determine whether the magnitudes of the force needed to push in and pull out the piston is identical. Of course, we usually assume they are identical, but that can be guaranteed only by empirical evidence.

Still, it is natural to expect that the quasistatic motion of the piston is reversible, if reactions are in equilibrium.

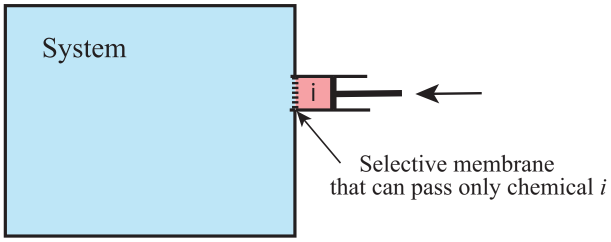

Figure 17.2: An operational definition of chemical potential

As can be seen from Gibbs' relation, it is possible to keep all work coordinates constant while pushing the piston, such as by suppressing the associated volume change.[277] Although how to add chemicals adiabatically to the system has already been discussed (→**4.15**), it is complicated. To avoid such procedures, as will be discussed in Section 18, we may use an isothermal process. $\Delta A = W - Q$ may be measured, where W is the work added to the system due to pushing in the chemical, and Q is the exchanged heat to keep the system temperature constant. Both are measurable. Therefore,

$$dA = -SdT + \boldsymbol{x}d\boldsymbol{X} + \mu_i dN_i + \cdots . \tag{17.6}$$

implying that $dA = \mu_i dN_i$ can be used to measure μ_i. However, the chemical potential obtained this way is a function of T and $\boldsymbol{Y}$ (not E and $\boldsymbol{Y}$).

17.8 The Gibbs-Duhem relation

Since $E = E(S, \{X_i\}, \{N_i\})$ is a first-degree homogeneous function (→**3.5**), (3.6) implies

$$E = S\frac{\partial E}{\partial S} + \sum_i X_i \frac{\partial E}{\partial X_i} + \sum_i N_i \frac{\partial E}{\partial N_i} = ST + \sum_i X_i x_i + \sum_i N_i \mu_i . \tag{17.7}$$

Taking the total differential of the above formula, we get

$$\begin{aligned} dE &= TdS + SdT + \sum_i (x_i dX_i + X_i dx_i) + \sum_i (\mu_i dN_i + N_i d\mu_i) & (17.8) \\ &= \left[TdS + \sum_i x_i dX_i + \sum_i \mu_i dN_i \right] + \left[SdT + \sum_i X_i dx_i + \sum_i N_i d\mu_i \right] . & (17.9) \end{aligned}$$

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[277] Notice that the chemicals pushed into the system can carry some other quantities such as 'magnetization' or 'electric charge.' If these properties are inseparable, it is not convenient to keep related work coordinates constant. Instead, the chemical potential should be extended to include these quantities as electric chemical potential we will see later.

However, we have Gibbs' relation (17.4), so this implies

$$SdT + \sum_i X_i dx_i + \sum_i N_i d\mu_i = 0.^{[278]} \tag{17.10}$$

This is called the *Gibbs-Duhem relation*. If there is only one chemical, this formula gives the differential of its chemical potential as

$$d\mu = -\frac{S}{N}dT - \sum_i \frac{X_i}{N}dx_i. \tag{17.11}$$

17.9 Chemical potential of an ideal gas

(17.11) reads for an ideal gas

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP = -\frac{S}{N}dT + \frac{RT}{P}dP \tag{17.12}$$

due to the equation of state $PV = NRT$. Therefore, if the temperature is constant we can integrate this as

$$\mu(T, P) = \mu(T, P^{\ominus}) + RT \log \frac{P}{P^{\ominus}} \tag{17.13}$$

In particular, if the chemical potential at the standard pressure $P^{\ominus} = 1$ (in chemistry, pressure is often measured in atm, and this implies $P^{\ominus} = 1$ atm) is $\mu(T, P^{\ominus}) = \mu^{\ominus}(T)$, then we may write

$$\mu(T, P) = \mu^{\ominus}(T) + RT \log P. \tag{17.14}$$

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[278] We are aware that there are many equivalent choices of materials coordinates. For example, $\boldsymbol{N}$ in this formula may be replaced with $\tilde{\boldsymbol{N}}$ as

$$SdT + \sum_i X_i dx_i + \sum_i \tilde{N}_i d\mu_i = 0.$$

This is apparently identical to the conventional formula in terms of chemical composition variables. However, in this formula $\tilde{N}_i$ is a particular value of the materials coordinate N_i, and is *not* a variable. In terms of the conventional variables (i.e., chemical composition variables) we cannot write the Gibbs-Duhem relation, simply because these variables are not independent from other variables (e.g., work coordinates), and also from other chemicals, either.

17.10 Dalton's law of partial pressures

The pressure of a mixture of two distinct gases 1 and 2 with mole numbers N_1 and N_2, respectively, is given by

$$P = (N_1 + N_2)RT/V, \tag{17.15}$$

if we assume both gases are ideal. Dalton understood this formula as the sum of the 'partial pressures' of individual gases, denoted by P_1 and P_2 respectively as $P = P_1 + P_2$:

$$P_1 = N_1RT/V, \tag{17.16}$$

$$P_2 = N_2RT/V. \tag{17.17}$$

This is called Dalton's *law of partial pressures.* If we introduce the *mole fraction* x of gas 1 as

$$x = \frac{N_1}{N_1 + N_2}, \tag{17.18}$$

the partial pressures read

$$P_1 = xP, \;\; P_2 = (1 - x)P. \tag{17.19}$$

17.11 Understanding partial pressures in terms of selective membranes

Partial pressure may be understood as follows (Fig. 17.3). Assume the temperature is constant.

Let the mole numbers of component gases 1 and 2 be N_1 and N_2, respectively. Under pressure P their volumes are $V_1 = xV$ and $V_2 = (1-x)V$, respectively, where x is the mole fraction of gas 1. The sum $V_1 + V_2$ is exactly V as illustrated in Fig. 17.3A. Assuming that the containers are adiabatic, we allow each gas to freely expand to volume V as Fig. 17.3B. Since the temperature does not change, the pressures are P_1 and P_2 in **17.10**, respectively. If we 'superpose' these two gases (B→C→D), the pressure in D is $P = P_1 + P_2$, since they do not interact.

Fig. 17.3 A: Let the mole numbers of the component gases 1 (green) and 2 (red) be N_1 and N_2, respectively. The individual volumes are $V_1 = xV$ and $V_2 = (1 - x)V$, respectively, and the total volume is exactly V. If we remove the separating wall between 'green' and 'red' and wait for equilibration, the resulting mixture of ideal gases is shown in D. The temperature does not change.

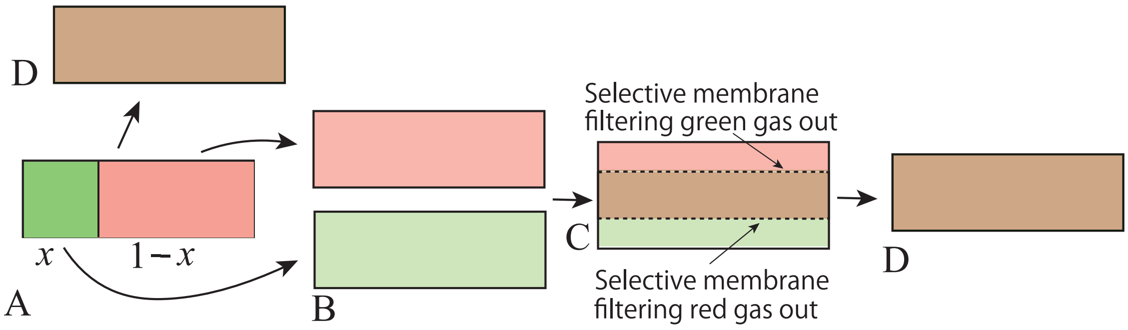

Figure 17.3: Dalton's law of partial pressures

If we use the selective membranes, Dalton's law of partial pressures may be understood in terms of the adiabatic free expansion of the gases.
B: If we adiabatically and freely expand each gas in the compartments of A to volume V, each will become a gas with its corresponding partial pressure.
C: Replace the bottom wall of the box with the red gas (resp., the upper wall of the box with the green gas) with a selective membrane that excludes the red gas (resp., the green gas) and merge the two boxes quasistatically. Since two gases do not interact, no work is needed for the merging process B→D. Thus, the total internal energy is constant throughout the process.

Needless to say, we assume that the processes using selective membranes are reversible, but the assumption is valid by the definition of the selective membranes (→**17.5**).

17.12 Mixing entropy

Mixing two substances usually makes the substances hard to separate, so our common sense tells us that the process A→D in Fig. 17.3 is irreversible. Indeed, A→B in A→B→C→D is irreversible due to the free expansion, so the entropy of the whole system should increase by the process A→D. This increase of entropy is called the *mixing entropy*. The process B→C→D is reversible thanks to the selective membranes, this entropy increase should be due to the process A→B (see Remark below).

The entropy of an ideal gas (i.e., the fundamental equation of an ideal gas) is given by (11.26). Adiabatic free expansion keeps the internal energy, so the system temperature does not change. Therefore, the fundamental equation tells us that for the N mole of an ideal gas the entropy change due to the volume change $V \to V'$ is given by

$$S(V') = S(V) + NR\log\frac{V'}{V}. \tag{17.20}$$

Therefore, for gas 1 and gas 2 the entropy changes are given by

$$S_{1\mathrm{B}} = S_{1\mathrm{A}} - N_1R\log x, \tag{17.21}$$

$$S_{2\mathrm{B}} = S_{2\mathrm{A}} - N_2R\log(1-x), \tag{17.22}$$

respectively, and the total entropy change reads

$$\Delta S = -NR\{x\log x + (1-x)\log(1-x)\}, \tag{17.23}$$

where the total mole number is written as $N = N_1 + N_2$.

Remark As we have seen, the mixing itself is a reversible process if performed quasistatically. Therefore, some authors assert that the irreversibility of the mixing process is due to diffusion (i.e., the expansion through other materials). However, the irreversibility is between A and B in Fig. 17.3. Thus, even 'diffusion' through something is irrelevant. The crux of mixing entropy is simply the irreversible expansion. Notice that this is consistent with **4.3** (I). See also the last paragraph of **17.16**.

17.13 Raoult's law and ideal liquid mixtures

Consider a mixture of liquid A and liquid B at temperature T. The liquids have vapor pressures (→**19.9** for the definition) $P_{\mathrm{A}0}$ and $P_{\mathrm{B}0}$, respectively, at T, when they are pure. Raoult found for many liquid mixtures, approximately:

> The vapor pressure of the mixture is the sum of individual partial pressures given by $P_{\mathrm{A}} = xP_{\mathrm{A}0}$ and $P_{\mathrm{B}} = (1-x)P_{\mathrm{B}0}$, where x is the mole fraction of A in the liquid mixture.

This empirical law is called *Raoult's law.*

The liquid mixture for which Raoult's law hold exactly is called an *ideal liquid mixture.*

17.14 The chemical potentials of the components of an ideal liquid mixture

Let us write the chemical potentials of pure liquids A and B at temperature T and pressure 1 (atm) be $\mu_{\mathrm{A}}^{\ominus}$ and $\mu_{\mathrm{B}}^{\ominus}$. Also let us write the chemical potentials of vapor A and vapor B at temperature T and pressure 1 (atm) be $\mu_{\mathrm{AG}}^{\ominus}$ and $\mu_{\mathrm{BG}}^{\ominus}$, respectively. If we assume the vapors are ideal gases, their chemical potentials have the form of (17.14), so the equilibrium relation for each component between the liquid and the vapor phases read, as given in **17.9**,[279]

$$\begin{aligned} \mu_{\mathrm{A}}^{\ominus} &= \mu_{\mathrm{AG}}^{\ominus} + RT\log P_{\mathrm{A0}}, & (17.24)\\ \mu_{\mathrm{B}}^{\ominus} &= \mu_{\mathrm{BG}}^{\ominus} + RT\log P_{\mathrm{B0}}, & (17.25) \end{aligned}$$

where P_{A0} and P_{B0} are the vapour pressures of liquid A and liquid B, respectively, at temperature T as in **17.13**. If we denote the chemical potentials of the components in the mixture as μ_{A} and μ_{B}, respectively, each component must be in equilibrium with the corresponding vapor component with its partial pressure:

$$\begin{aligned} \mu_{\mathrm{A}} &= \mu_{\mathrm{AG}}^{\ominus} + RT\log(xP_{\mathrm{A0}}), & (17.26)\\ \mu_{\mathrm{B}} &= \mu_{\mathrm{BG}}^{\ominus} + RT\log((1-x)P_{\mathrm{B0}}). & (17.27) \end{aligned}$$

Comparing the above two sets of equations, the chemical potentials of the components may be given by

$$\begin{aligned} \mu_{\mathrm{A}} &= \mu_{\mathrm{A}}^{\ominus} + RT\log x, & (17.28)\\ \mu_{\mathrm{B}} &= \mu_{\mathrm{B}}^{\ominus} + RT\log(1-x). & (17.29) \end{aligned}$$

A mixed liquid with these component chemical potentials is called an *ideal liquid mixture.*

17.15 Mixing entropy of ideal liquids

(17.7) tells us, generally for a two component liquid mixture,

$$E = ST - PV + \mu_{\mathrm{A}}N_{\mathrm{A}} + \mu_{\mathrm{B}}N_{\mathrm{B}}. \tag{17.30}$$

Before mixing the two components, the term $\mu_{\mathrm{A}}N_{\mathrm{A}} + \mu_{\mathrm{B}}N_{\mathrm{B}}$ reads

$$xN\mu_{\mathrm{A}}^{\ominus} + (1-x)N\mu_{\mathrm{B}}^{\ominus}, \tag{17.31}$$

---

[279] In the following formulas, precisely speaking, the chemical potentials of the pure liquids must be at their respective vapor pressures (→**19.9**), but the chemical potential of the ordinary liquid is insensitive to the pressure if it is not very high (say, 10 atm).

where $N = N_A + N_B$. After mixing, we have

$$xN[\mu_A^{\ominus} + RT\log x] + (1-x)N[\mu_B^{\ominus} + RT\log(1-x)]. \tag{17.32}$$

For ideal liquids, it is assumed that mixing does not change the internal energy or volume, so the entropy change ΔS reads, under the constant temperature-pressure condition,

$$T\Delta S = -\Delta(\mu_A N_A + \mu_B N_B). \tag{17.33}$$

Comparing (17.31) and (17.32), we conclude

$$\Delta S = -NR[x\log x + (1-x)\log(1-x)], \tag{17.34}$$

which is the increase in entropy due to mixing and is called the mixing entropy. Notice that this formula is exactly the same as the one for ideal gas mixing case (17.23).

17.16 Meaning of the mixing entropy

For simplicity, we consider a one-to-one mixing, i.e., the $x = 1/2$ case.

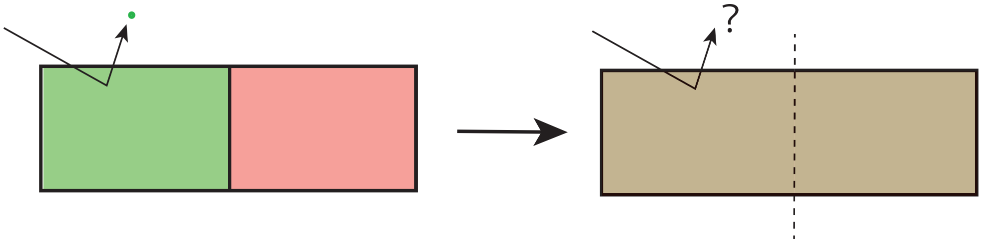

Figure 17.4: Experiment to eject a particle from a one-to-one mixture

Let us consider an experiment to eject a particle from the left half of the system[280] (Fig. 17.4). Before mixing, always green particles are detected; we know this even before performing any experiments. But, what about after mixing? We would

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[280] According to the official standpoint of thermodynamics, we do not (cannot) inquire whether a substance is made of particles or not. However, it is a macroscopic fact that if a macroscopic object is irradiated by appropriate beam, particles are ejected. We cannot know the 'actual' structure of the object—even for a gas; it must be quite different from the collection of flying ball bearings. In reality, nobody knows what is going on.

Note that we are only using a macroscopically verifiable fact here: if we mix similar substances with a definite mole ratio, and then eject a particle, the probability to get a particular molecular species is proportional to the mole fraction.

detect both red and green particles evenly, so we cannot predict the outcome of each experimental run (Fig. 17.4Right).

What question should we ask to know the outcome of a particular run? We have only to make one question that can be answered by YES or NO: “Is it green?”[281] By “mixing,” what we knew without asking any questions becomes uncertain, and we need to obtain new knowledge that can be obtained from a single YES-NO question to restore “perfect knowledge” about the system.

The required knowledge may be quantitated by the number of questions to obtain it. The amount of knowledge we can obtain from a single unbiased YES-NO question (called the *information* we can obtain) is called ‘1 bit of information’.

For the case with $x = 1/2$, the mixing entropy is given by $\Delta S = NR\log 2$. To obtain complete information about the left half, we must keep asking the question till the half becomes empty. How many times must we ask? Since 1 mole is exhausted if ejection experiments are repeated N_A (Avogadro’s constant) times, through the mixing process we lose NN_A bits of information. This means entropy per particle $NR\log 2/NN_A = k_B \log 2$ corresponds to 1 bit, where k_B is the *Boltzmann constant.*

Next, let us consider doubling the volume of a gas by adiabatic free expansion (Fig. 17.5). Once again, we will consider particle ejection experiments.

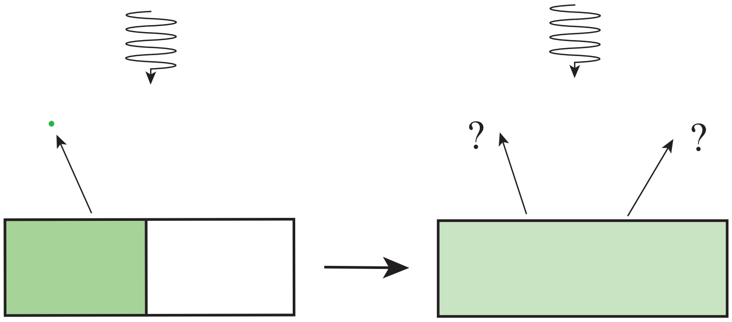

Figure 17.5: Doubling the volume of a gas by adiabatic free expansion

Before the volume is doubled, particles always come out from the left side, but af-

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[281] It goes without saying that the answer to the YES or NO question must be totally unpredictable (‘*unbiased YES-NO question*’). However, is the condition “totally unpredictable” a perfectly unambiguous prerequisite? There is ambiguity here, because ‘randomness’ is a tricky concept, usually, for example, tied to the total symmetry of the space.

It is often said that randomness is guaranteed only by quantum mechanics, but this depends on its theoretical structure and Born’s probability interpretation. The assertion is a convention; it osund obvious for some according to their world view.

ter doubling the volume, we cannot predict whether a particle will come out from the left or the right half. In this case, we have lost the information that could be obtained from a single unbiased YES-NO question, “Is it from the left?”. Notice that the entropy increase is exactly the same as the above mixing problem: $\Delta S = NT \log 2$.

These two examples teach us two lessons:
The entropy increase due to a process looks quantitatively connected to the amount of knowledge we need to describe the system after the process as precisely as before the process. Additionally, as noted before (→**17.12**), the entropy increase by mixing is solely due to expansion.

17.17 Entropy and phase transition

Phase transitions and related topics will be discussed in detail later (Section 23). For now, let us consider the changes we encounter daily such as freezing of water or boiling to produce water vapor. Such changes are called phase transitions. For water liquid phase (water coming out of a faucet), gas phase (vapor) and sold phase (ice) are distinct at our daily temperature and pressure. During phase transitions, water exchanges the so-called *latent heat* such as melting heat or boiling heat with its environment.

Let L be the latent heat absorbed by the system when it turns from phase A to phase B, then the entropy change due to the phase transition A→B is given by

$$\Delta S_{\mathrm{A}\to\mathrm{B}} = \frac{L}{T}. \tag{17.35}$$

For example, 1 mole of ice melts at 0 °C = 273 K under 1 atm to become liquid water. The latent heat is 5940 J/mole. Therefore, 1 mole of liquid water at 0 °C has a larger entropy by $\Delta S = 6010/273 = 22.0$ J/K·mol $= 2.65R$ ($R = 8.314$ J/K·mol) than 1 mole of ice. What does this mean from the information standpoint?

As we have seen in **17.16** 1 bit/molecule corresponds to entropy change of $R \log 2 = 0.693R$ J/K per mole. Therefore, the melting entropy is $2.65/0.693 \approx 3.8$ bits/molecule. To understand the state of a single molecule in liquid water as accurately as in ice, we must ask about 4 more YES-NO questions.[282]

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[282] If we may use a detailed molecular model, this number may be interpreted as follows: in cold water a water molecule still cannot move freely due to hydrogen-bonding networks, but can rotate relatively freely than in a crystal. To specify its rotation axis by its residing octant, we already need 3 bits.

18 Isothermal process and Legendre-Fenchel transformation

18.1 Thermodynamics of isothermal processes

A process in which initial and the final states have the same temperature is called an *isothermal process*. As is usual in thermodynamics, we do not care whatever happens during the process. To begin with during the process the system need not be in equilibrium, so even mentioning temperatures during the process is meaningless. However, the most practical way to achieve an isothermal process is to maintain the system in thermal contact with a heat bath. This guarantees that the initial and the final equilibrium states are at the same temperature; Of course, we cannot say anything about the system temperature in between, even if the system remains in thermal contact with a heat bath of temperature T.

To utilize thermodynamics we must connect the intial and the final states with a reversible quasistatic process. For isothermal processes it is convenient to devise an appropriate reversible quasistatic isothermal process. Let us consider Gibbs' relation (→**17.6**) for an isothermal process. To keep the system temperature, free exchange of heat between the system and its environment should be allowed, so instead of dE, we should consider

$$dE - dQ = dW + dZ = \sum y_i dY_i = \sum x_i dX_i + \sum \mu_i dN_i. \tag{18.1}$$

Reversibly and quasistatically $dQ = TdS$ and the system temperature T is constant. Therefore, it is convenient to rewrite (18.1) as

$$dE - TdS = d(E - TS) = dW + dZ = \sum x_i dX_i + \sum \mu_i dN_i. \tag{18.2}$$

Thus, to introduce

$$A = E - TS, \tag{18.3}$$

called the *Helmholtz energy*, is convenient. For isothermal reversible quasistatic processes (17.1) implies

$$dA = dW + dZ. \tag{18.4}$$

Here, just as dQ previously, dW and dZ are symbols for 1-forms and do not imply exact forms (→**9.9**).

If the system is materially closed without the dZ term, $dA = dW$, so (as adiabatic processes[283]) quasistatic work form is exact for isothermal processes.

18.2 The change of Helmholtz energy for isothermal but not quasistatic processes: work principle

First, let us consider a closed system (thus there is no Z, although chemical reactions or chemical equilibrium shifts may occur in the system). For isothermal reversible quasistatic processes (18.4) implies

$$\Delta A = W, \tag{18.5}$$

where W is the work done to the system from outside reversibly and quasistatically.

What happens, if the work is not reversible and generally involves some dissipation (in the system)? Naturally, the system heats up, but the generated heat would escape to the attached heat bath. That is, not all the added work is converted to the system energy:

$$\Delta A \le W. \tag{18.6}$$

This is called the *principle of minimum work*. That is, to cause a given change ΔA the minimum work specified by (18.5) is possible if the work is added reversibly.

If a system does work on the external world, if that is done without loss (i.e., reversibly without dissipation) the maximum work should be taken out. This is called the *maximum work principle*. In this case A is reduced, and the system loses energy as work, so both ΔA and W are negative according to our sign convention. The argument (18.6) is algebraic, so it should always be correct. Therefore,

$$|\Delta A| \ge |W|. \tag{18.7}$$

This is the maximum work principle: we can take out the largest work if reversible.

For the general cases with mass actions (that is, for the system being no more closed), we have only to replace W with $W + Z$:

$$\Delta A \le W + Z. \tag{18.8}$$

If there is no work, but chemical energy could be extracted by chemical reactions, we have $|\Delta A| \ge |Z|$ as (18.7). However, in practice, not only the constant temperature, but also the constant pressure condition becomes important. This topic will be postponed to the section discussing the Gibbs energy (→**19.6**).

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[283] However, as seen in **7.7**, for adiabatic processes work form (if defined) becomes exact for any adiabatic process (need not be quasistatic).

18.3 Clausius' inequality and work principle

The derivation of the work principle in **18.2** may be admissible in physics, but it may not sound like a formal demonstration. Therefore, here, the principle is rederived by using Clausius' inequality (→**14.4**). To realize an isothermal process, we may assume that the system is always in thermal contact with a heat bath at a constant temperature T. Needless to say, the system may not be in equilibrium during the process, so its temperature may be meaningless. If we apply Clausius' inequality

$$\Delta S \geq \frac{Q}{T} \tag{18.9}$$

to $Q = \Delta E - W$, we have

$$T\Delta S = \Delta(TS) \geq \Delta E - W \ \ \Rightarrow\ W \geq \Delta(E - TS) = \Delta A. \tag{18.10}$$

This is just (18.6).

18.4 Helmholtz energy minimization principle

If a closed system does not exchange work with its environment, the inequality (18.6), which holds under constant temperature, reads

$$\Delta A \leq 0. \tag{18.11}$$

That is, under constant temperature, if a change can actually happen without any external net contribution of operational coordinate change, then its Helmholtz energy should decrease. This implies that the intial state of the system was actually not an equilibrium state. That is, if we can apply thermodynamics to the system

$$\Delta A \geq 0 \tag{18.12}$$

must hold. Here Δ implies the result of a thermodynamic variation under constant T. That is, just as **12.6** but defined as follows with the constant T condition: For a function of T and operational coordinates $J(T, \boldsymbol{Y})$,

$$\Delta J(T, \boldsymbol{Y}) = \sum_{i \in \mathcal{P}} J(T, \boldsymbol{Y}_i) - J(T, \boldsymbol{Y}), \tag{18.13}$$

where $\mathcal{P}$ denotes the set of subsytems by a particular partition of the original system into subsystems, and $\boldsymbol{Y} = \sum_{i\in\mathcal{P}} \boldsymbol{Y}_i$.[284]

For any equilibrium state under constant temperature (18.12) must hold. This is called the *Helmholtz energy minimization principle*, which is a global principle for a state to be in equilibrium. (18.12) is just a Jensen's inequality, because A under constant T is a convex function of $\boldsymbol{Y}$, simply because so is E (→**13.9**).

18.5 Legendre transformation

The transformation: $E \to A = E - ST$ is called the *Legendre transformation*, which changes the independent variables $S, \boldsymbol{X}, \boldsymbol{N}$ of E to $T, \boldsymbol{X}, \boldsymbol{N}$. Certainly,

$$dE = TdS + \boldsymbol{x}d\boldsymbol{X} + \boldsymbol{\mu}d\boldsymbol{N} \;\Rightarrow\; dA = -SdT + \boldsymbol{x}d\boldsymbol{X} + \boldsymbol{\mu}d\boldsymbol{N}. \tag{18.14}$$

However, the formula alone does not explain the meaning of the Legendre transformation at all.

When we write

$$E(S, \boldsymbol{X}, \boldsymbol{N}) \to A(T, \boldsymbol{X}, \boldsymbol{N}) = E(S, \boldsymbol{X}, \boldsymbol{N}) - TS,$$

the T in the formula is not arbitrary but is determined by $E(S, \boldsymbol{X}, \boldsymbol{N})$:[285]

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},\boldsymbol{N}}. \tag{18.15}$$

Let us consider the relationship between E and A geometrically. Since the other variables are unaffected, let us suppress $\boldsymbol{X}, \boldsymbol{N}$ from now on.

Consider a state whose entropy is given by the green dot (Fig. 18.1). Its temperature T is the slope of the tangent line to E at that point, since E is a (monotone

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[284] Here, we consider only simple systems, but generalizing our discussion to compound systems is just as discussed before in **12.6** .

[285] **Warning.** Recall that the following partial derivative makes sense, only when there are no chemical reactions in the system, if we adopt the conventional expression of the amounts of chemicals in the system. Thus, conventional thermodynamics textbooks (if honest) clearly state that chemical reactions can be freely stopped/frozen at will. The following differentiation is computed while all the reactions are frozen. What is a logical consequence? If you follow existing thermodynamic textbooks, the use of Legendre-Fenchel transformation is not permitted in the presence of chemical reactions: Hence, free energies such as Gibbs energy cannot be used in chemical thermodynamics.

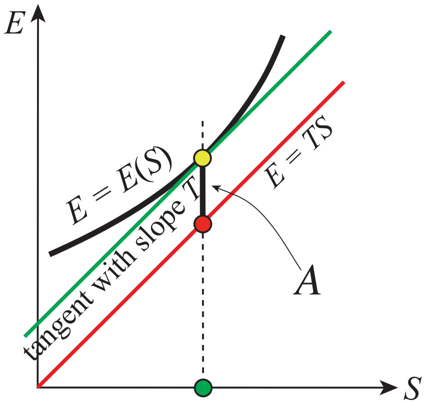

Figure 18.1: Legendre transformation

increasing) convex function of S (→**??**). Draw a line (red line) with the same slope passing through the origin, $E = TS$. Then, $A = E - TS$ is the E-coordinate value of the yellow dot subtracted that of the red dot. This implies that the minimum of the (signed) distance measured along the E-axis of the curve $E = E(S)$ and the line $E = TS$ is A. Thus, we have the following expression (the conditions are written to the right of a vertical bar):

$$A = \min_S |_{\boldsymbol{Y}} [E(S, \boldsymbol{Y}) - TS]. \tag{18.16}$$

The suffix $\boldsymbol{Y}$ to the right of | implies that the minimum $\min_S$ is taken under the condition that the operational coordinates are fixed. Since E is differentiable with respect to S, the conditional minimization indeed gives

$$\left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{Y}} - T = 0, \tag{18.17}$$

so (18.16) agrees with the elementary Legendre transformation.

Now, rewrite (18.16) as

$$-A = \max_S |_{\boldsymbol{Y}} [TS - E(S, \boldsymbol{Y})]. \tag{18.18}$$

Since E is a convex function, in particular, a convex function of S, this formula is just the (partial) *Legendre-Fenchel transformation* (→**18.6**, **18.7**).

From now on, in these notes any Legendre transformation will be discussed as the Legendre-Fenchel transformation partly to emphasize that transformation is a tool of convex analysis (→**13.1**) and that the differentiability of functions is not required. The second point is crucial when we discuss phase transitions (→**23.11**).

18.6 Legendre-Fenchel transformation

For a convex function $f : \mathbb{R}^n \to \mathbb{R}$ (→**13.2**)

$$f^*(x) = \sup_y [x \cdot y - f(y)] \tag{18.19}$$

is called the *conjugate function* of f. [Here, sup and max may not be fastidiously distinguished.[286]] The transformation $f \to f^*$ is called the *Legendre-Fenchel transformation*. If f is everywhere differentiable, as we have seen in **18.5**, Legendre-Fenchel transformations agree with the conventional Legendre transformation.

Pay special attention to the following two theorems

(1) The conjugate function f^* of a convex function f is convex. [Proof →**18.9**]

(2) The conjugate of the conjugate of a convex function is the original convex function: $(f^*)^* = f^{**} = f$. [Proof→**18.10**]

These two theorems imply for E and A:

(1) $-A$ is a convex function of T (That is, A is convex upward as a function of T).

(2) If we know A, we can completely recover E.

Remark. Legendre-Fenchel transformation is a standard terminology in convex analysis. Although non-differentiable cases are also discussed under Legendre transformation these days, the use in partial differential equations and mechanics (symplectic dynamics) is traditionally restricted to differentiable cases as the original Legendre transformation. As seen in **23.11** the applications to nondifferentiable cases are essential to understanding phase transitions (→**23.11**). To guarantee the completeness (→**18.12**) of thermodynamic functions this generalization is crucial, and hence the name 'Legendre-Fenchel transformation' will be used throughout these notes.

18.7 Partial Legendre-Fenchel transformation

As we have already seen in **18.5**, the Legendre-Fenchel transformation of E to A is

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[286] ⟪**sup and max**⟫ 'max' denotes the maximum value. $M = \max_{y \in C} f(y)$ implies that the function f assumes at a point in C actually the largest value M. In contrast, $M = \sup_{y \in C} f(y)$ implies that M is the least upper bound of the values of f on C (that is, the least upper bound of the set $f(C)$ is M), so there need not actually be a point in C where f takes the value M. For example, on $C = (-1, 1)$ for $f(y) = 1 - y^2$ $\max_{y \in C} f = \sup_{y \in C} f = 1$, but for $g = y^2$ there is no $\max_{y \in C} g(y)$. Still, $\sup_{y \in C} g(y) = 1$, so sup and max must be distinguished, but for many cases we will discuss, max exists intuitively, so we may consider sup as max.

with respect to the variable S and its conjugate T. No other variables are involved. Such transformation should be called a *partial Legendre-Fenchel transformation*. Its mathematics is almost the same as is explained in **18.6**: we fix all the remaining variables, and at each fixed value, we can define its Legendre-Fenchel transformation. We will use the following notation (as already used):

$$f^*(x,z) = \sup_y|_z[x \cdot y - f(y,z)]. \tag{18.20}$$

Its inverse transformation is

$$f(y,z) = \sup_x|_z[x \cdot y - f^*(x,z)]. \tag{18.21}$$

18.8 What happens if E is totally Legendre-Fenchel transformed?

In thermodynamics, the Legendre-Fenchel transformation is always with respect to a genuine subset of the thermodynamic coordinates (→**18.7**). Since E is a first-degree homogeneous function (→**3.5**) of extensive variables, obviously we have

$$0 = \sup_{S,\boldsymbol{Y}}[ST + \boldsymbol{y} \cdot \boldsymbol{Y} - E], \tag{18.22}$$

which may seem like a meaningless result, but is it? Since 0 is obviously a convex function, $f^{**} = f$ (→**18.6** (ii)) implies $0^* = E$:

$$E = \sup_{T,\boldsymbol{y}}[ST + \boldsymbol{y} \cdot \boldsymbol{Y}]. \tag{18.23}$$

This formula implies that if all the extensive quantities are measured, the most important thermodynamic quantity can be determined. Thus, an apparently self-evident formula (18.22) could be regarded as a foundation of thermodynamics.

18.9 Conjugates of convex functions are convex

As the following computation demonstrates, if f^* is defined as (18.19), whatever f may be, f^* satisfies Jensen's inequality (→**13.3**), so it is convex. For any $\lambda \in [0,1]$

$$\begin{aligned}
\lambda f^*(x_1^*) + (1-\lambda) f^*(x_2^*) &= \lambda \sup_{x_1}[x_1 \cdot x_1^* - f(x_1)] + (1-\lambda)\sup_{x_2}[x_2 \cdot x_2^* - f(x_2)] \\
&= \sup_{x_1,x_2}\{\lambda[x_1 \cdot x_1^* - f(x_1)] + (1-\lambda)[x_2 \cdot x_2^* - f(x_2)]\} \\
&\geq \sup_{x_1=x_2}\{\lambda[x_1 \cdot x_1^* - f(x_1)] + (1-\lambda)[x_2 \cdot x_2^* - f(x_2)]\} \\
&= \sup_x\{\lambda[x \cdot x_1^* - f(x)] + (1-\lambda)[x \cdot x_2^* - f(x)]\} \\
&= \sup_x[x \cdot (\lambda x_1^* + (1-\lambda)x_2^*) - f(x)] \\
&= f^*(\lambda x_1^* + (1-\lambda)x_2^*).
\end{aligned} \tag{18.24}$$

Therefore, f^* is convex irrespective of f. In particular, the conjugate of a convex function is again convex.

18.10 $f^{**} = f$, if f is convex

Let $f : \mathbb{R}^n \to \mathbb{R}$ be a convex function. Then, $f^{**} = f$.

By definition for $\forall x$ and for $\forall y$

$$f^*(x) \geq x \cdot y - f(y). \tag{18.25}$$

If f is convex, then for each y there is x such that the equality holds.[287] Therefore, in the inequality below left for each y there is x satisfying the equality. That is, the equation in the right holds:

$$f(y) \geq x \cdot y - f^*(x) \;\Rightarrow\; f(y) = \sup_x [x \cdot y - f^*(x)]. \tag{18.26}$$

This is the definition of f^{**}, and implies $f^{**} = f$.

18.11 Helmholtz energy in terms of Legendre-Fenchel transformation: general case

Let us rewrite (18.16) as

$$-A(T) = \max_S |_{\boldsymbol{Y}} [TS - E(S, \boldsymbol{Y})] = \sup_S |_{\boldsymbol{Y}} [TS - E(S, \boldsymbol{Y})]. \tag{18.27}$$

Since $E(S)$ is convex, the above formula is a (partial) Legendre-Fenchel transformation **18.6** (or **18.7**) of a convex function. That is,

$$-A = E^*. \tag{18.28}$$

Thus, we immediately know that $-A$ is a convex function of T; $A(T)$ is a concave function of T, Also, we have

$$(-A)^* = E^{**} = E. \tag{18.29}$$

More explicitly, this reads

$$E = \sup_T |_{\boldsymbol{Y}} [TS - (-A)] = \sup_T |_{\boldsymbol{Y}} [TS + A]. \tag{18.30}$$

The implication of this formula is important. $E = E(S, \boldsymbol{Y})$ is a function completely describing the thermodynamics of a given system (→**18.12**). Since Helmholtz energy A allows the construction of E as seen in (18.30), A is, though dependent on non-thermodynamic coordinate T, also a function that completely describes the thermodynamics of the system.

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[287] To understand this really intuitively we need geometry of a convex function and its supporting planes. This is explained in Appendix at the end of this section (→**D.2**).

If f is not convex, for each y there is no guarantee for x giving the equality to exist, so $f^{**} = f$ need not hold. As seen in **18.9**, f^{**} is convex and agrees with f where it is convex, so f^{**} is called the *convex hull* of f.

18.12 Complete thermodynamic functions

A thermodynamic function that can reconstruct or restore the internal energy $E = E(S, \boldsymbol{Y})$ as a function of S and operational coordinates $\boldsymbol{Y}$ through a Legendre-Fenchel transformation is called a *complete thermodynamic function*. The Helmholtz energy is an example as seen in **18.5**.

18.13 Gibbs-Helmholtz equation for the Helmholtz energy

Since the Helmholtz energy is a complete thermodynamic function **18.12**, there should be a formula obtaining the internal energy from the Helmholtz energy. Since $E = A + TS$ and $dA = -SdT + \boldsymbol{y}d\boldsymbol{Y}$,

$$E = A - T\left(\frac{\partial A}{\partial T}\right)_{\boldsymbol{Y}} = A + \frac{1}{T}\left(\frac{\partial A}{\partial 1/T}\right)_{\boldsymbol{Y}} = \left(\frac{\partial A/T}{\partial 1/T}\right)_{\boldsymbol{Y}}. \tag{18.31}$$

This formula is a rehash of (19.7) for the Gibbs energy.

D Appendix D: Geometrical meaning of the Legendre-Fenchel transformation

D.1 Convex functions are supported by hyperplanes from below

Let $f : \mathbb{R}^n \to \mathbb{R}$ be a convex function. Since its epigraph epi f (→**13.2**) is a convex set, there is a hyperplane $\mu = h(x) = x \cdot b - \beta$ below it. That is, we can choose $b \in \mathbb{R}^n$ and $\beta \in \mathbb{R}$ so that

$$f(x) \geq x \cdot b - \beta \tag{D.1}$$

holds.[288] See Fig. D.1 Left. In particular, for each b we can choose β as small as possible so that the hypersurface $y = x \cdot b - \beta$ touches epi$f$. A hyperplane tangent to epi f is called a *supporting hyperplane* of f. Thus, we see that the graph of f is enveloped by all the supporting hyperplanes of f itself (Fig. D.1Right). That is, f can be reconstructed from the totality of the parameters (b, β) characterizing the supporting hyperplanes of epi f (→**D.2**). This is the essence of the Legendre-Fenchel transformation **18.6**.

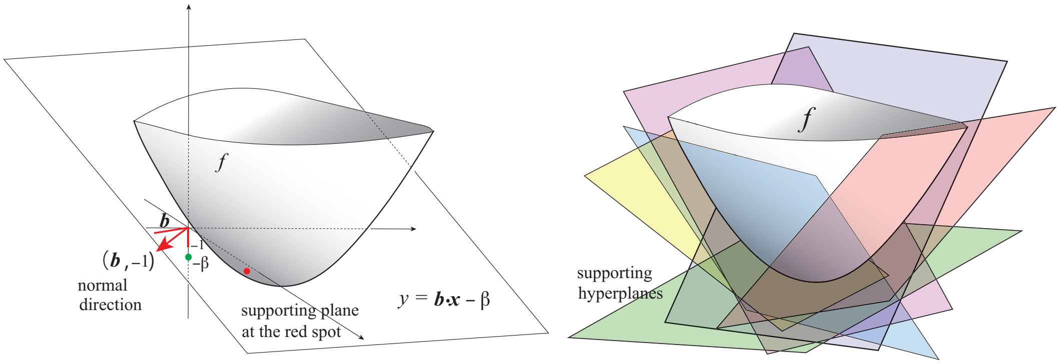

Figure D.1: Examples of supporting planes of f

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[288] Notice that $y = x \cdot b - \beta$ expresses a hyperplane in $\mathbb{R}^n \times \mathbb{R}$ passing through $(0, -\beta)$ and perpendicular to $(b, -1)$:

$$(b, -1) \cdot (x, y + \beta) = 0 \;\Rightarrow\; b \cdot x - y - \beta = 0 \;\Rightarrow\; y = b \cdot x - \beta. \tag{D.2}$$

D.2 Reconstruction of a convex function from its supporting planes

Let $f : \mathbb{R}^n \mapsto \mathbb{R}$ be a convex function. Let $\mu = x^* \cdot x - \mu^*$ be a hyperplane that has epi f on its upper side (allowing tangential contacts) and F^* be the set of totality of the parameters (x^*, μ^*) allowed for such hyperplanes:

$$F^* = \{(x^*, \mu^*)\} \,|\, f(x) \geq x^* \cdot x - \mu^* \text{ for } \forall x \in \mathbb{R}^n\}. \tag{D.3}$$

That this set is a closed convex set may be demonstrated as follows:
Suppose (x_1^*, μ_1^*) and (x_2^*, μ_2^*) belong to F^*. For $\forall x \in \mathbb{R}^n$

$$\begin{aligned} f(x) &\geq x_1^* \cdot x - \mu_1^*, & \text{(D.4)} \\ f(x) &\geq x_2^* \cdot x - \mu_2^*, & \text{(D.5)} \end{aligned}$$

so for any $\lambda \in [0, 1]$

$$f(x) \geq (\lambda x_1^* + (1-\lambda)x_2^*) \cdot x - (\lambda \mu_1^* + (1-\lambda)\mu_2^*). \tag{D.6}$$

holds. That is, $(\lambda x_1^* + (1-\lambda)x_2^*, \lambda \mu_1^* + (1-\lambda)\mu_2^*) \in F^*$.

For $\forall x \in \mathbb{R}^n$

$$f(x) \geq x^* \cdot x - \mu^*, \tag{D.7}$$

so for $\forall x \in \mathbb{R}^n$

$$\mu^* \geq x^* \cdot x - f(x) \tag{D.8}$$

holds. Therefore,

$$\mu^* \geq \sup_x [x^* \cdot x - f(x)]. \tag{D.9}$$

That is, $(x^*, \mu^*) \in F^*$ implies that this is the epigraph of f^* defined as

$$\mu^* \geq f^*(x^*) = \sup_x [x^* \cdot x - f(x)]. \tag{D.10}$$

or $F^* = \text{epi} f^*$. F^* is a closed convex set, so f^* is a convex function, which is the conjugate of f.

Notice that f^* is the upper bound of the affine function $g(x^*) = x \cdot x^* - \mu$ at each x^* under the condition: $(x, \mu) \in F = \text{epi} f$.

D.3 Gradient inequality

Let f be a convex function. If for $\forall z$ x^* satisfies

$$f(z) \geq f(x) + x^* \cdot (z - x) \tag{D.11}$$

for a given x, x^* is called the *subgradient* of f at x, and the inequality (D.11) is called the *subgradient inequality* (see Fig. D.2).

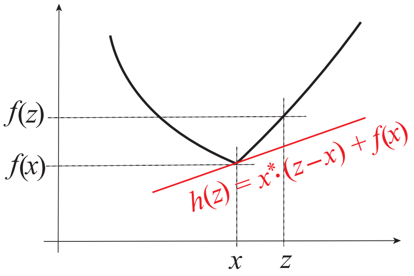

Figure D.2: Subgradient x^* and subgradient inequality illustrated

This inequality implies that the following affine function illustrated in Fig. D.2

$$h(z) = x^* \cdot (z - x) + f(x) \tag{D.12}$$

expresses the supporting hyperplane (→**D.1**) of epi$f$ that is in contact with it at $(x, f(x))$.

If f is not differentiable at x its subgradients are not unique. The totality of subgradients at x is called the *subdifferential* of f at x and is denoted as $\partial f(x)$.

If a convex function f is differentiable at x, (D.11) reads

$$f(z) \geq f(x) + \nabla f(x) \cdot (z - x). \tag{D.13}$$

Let us call this the *gradient inequality.*

D.4 A consequence of the gradient inequality

If we write (D.13) around x and around x', for any point z

$$f(z) \geq f(x) + \nabla f(x) \cdot (z - x), \tag{D.14}$$

$$f(z) \geq f(x') + \nabla f(x') \cdot (z - x'). \tag{D.15}$$

Therefore, we obtain

$$\begin{aligned} f(x') &\geq f(x) + \nabla f(x) \cdot (x' - x) \ \Rightarrow f(x') - f(x) \geq \nabla f(x) \cdot (x' - x), \quad \text{(D.16)} \\ f(x) &\geq f(x') + \nabla f(x') \cdot (x - x') \ \Rightarrow f(x) - f(x') \geq \nabla f(x') \cdot (x - x'). \quad \text{(D.17)} \end{aligned}$$

Adding these two inequalities we obtain

$$0 \geq \nabla f(x) \cdot (x' - x) + \nabla f(x') \cdot (x - x') = -(\nabla f(x) - \nabla f(x')) \cdot (x' - x). \quad \text{(D.18)}$$

That is, we have obtained

$$(\nabla f(x) - \nabla f(x')) \cdot (x - x') \geq 0. \quad \text{(D.19)}$$

If we apply this to E, we get an inequality for differences between any two points in the thermodynamic space:

$$\Delta S \Delta T + \sum \Delta x_i \Delta X_i + \sum \Delta \mu_i \Delta N_i \geq 0. \quad \text{(D.20)}$$

19 Constant temperature-pressure processes and Gibbs energy

19.1 Thermodynamics of isothermal and isobaric processes

Experiments are often conducted in environments with constant temperature and pressure due to their relative ease. For systems in which chemical reactions are of primary interest, Gibbs' relation may be written as

$$dE - TdS + PdV = d(E - TS + PV) = \sum_{V^c} x_i dX_i + \sum_i \mu_i dN_i, \tag{19.1}$$

where $\sum_{V^c} x_i dX_i$ denotes the works other than the volume work. Therefore, similar to the case of Helmholtz energy (→**18.1**), it is convenient to define the *Gibbs energy* as

$$G = E - TS - (-P)V = E - TS + PV. \tag{19.2}$$

This is also a Legendre transformation as the Helmholtz energy in elementary thermodynamics. To make its mathematical properties explicit the following Legendre-Fenchel transformation is recommended (→**18.6**, **18.7**):

$$-G = \sup_{S,V}|_{\boldsymbol{Y}\setminus V}\,[TS + (-P)V - E]. \tag{19.3}$$

The conditions (what to keep const, etc.) are written after |. Do not forget that the conjugate of V is $-P$. From the general theory of the Legendre-Fenchel transformation (→**18.6**) $-G$ is a convex function of T, P (while keeping all the work coordinates other than V fixed under a materially closed condition). Therefore, we can recover E:

$$E = \sup_{T,P}|_{\boldsymbol{Y}\setminus V}\,[ST + (-P)V - (-G)] = \sup_{T,P}|_{\boldsymbol{Y}\setminus V}\,[TS - PV + G]. \tag{19.4}$$

This is similar to the case of A (→**18.11**). Therefore, G is also a complete thermodynamic function (→**18.12**).

19.2 Results of partial Legendre-Fenchel transformation

E is a convex function[289] of S, $\boldsymbol{X}$ and $\boldsymbol{N}$. If we Legendre-Fenchel-transform E with

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[289] if there are no non-additive extensive quantities

respect to S, the resulting $-A$ is a convex function of T if all other variables are fixed under materially closed conditions. Although E is a convex function of all its variables, A is concave only with respect T; if T is fixed, as a function of $\boldsymbol{X}$ it is a convex function; A itself is neither convex nor concave.

A similar remark applies to G. $-G$ is a convex function of T and P, which means G is a two-variable concave function of T and P when all the operational coordinates are fixed except for V; G itself is neither a convex nor convex function.

19.3 Enthalpy

The Legendre-Fenchel transformation in **19.1** may be understood in two steps; first the transformation with respect to V, then with respect to S:

$$-H = \sup_V |_{S,\boldsymbol{Y}\setminus V}[-PV - E], \tag{19.5}$$

$$-G = \sup_T |_{P,\boldsymbol{Y}\setminus V}[TS - H]. \tag{19.6}$$

Combine these two equations gives us (19.3). H is called the *enthalpy*. It is a complete thermodynamic function, since inverse transformation(s) recovers E. Under a constant pressure condition, ignoring the exchange of energy due to volume change, the remaining energy change is ΔH. For an ordinary chemical experiment in a lab, this corresponds to the exchange of heat due to chemical reactions (the *reaction heat*).

Comparing (19.6) and (18.27) we get the equation corresponding to (18.31):

$$H = \left(\frac{\partial G/T}{\partial 1/T}\right)_{P,\boldsymbol{Y}\setminus V}. \tag{19.7}$$

This is the *Gibbs-Helmholtz equation*, which allows us to calculate the Gibbs energy change from the reaction heat.

19.4 Chemical potential and Gibbs energy

In chemistry there are often no work coordinates other than volume V. This means that there is no work contribution to the system other than the volume work. Thus, we have

$$dG = -SdT + VdP + \sum_i \mu_i dN_i. \tag{19.8}$$

Therefore, under constant temperature and pressure we have

$$dG = \sum_i \mu_i dN_i. \tag{19.9}$$

Consequently, if we add a chemical under constant temperature and pressure following the procedure illustrated in Fig. 17.2, the required work $\mu_i dN_i$ should directly give its chemical potential. However, note that, in contrast to the one explained in **17.7**, its independent variables are T and P.

The meaning of the materials coordinate (→**4.9**) change dN_i is that the experimenter adds dN_i moles of chemical i to the system. Since this addition may be through a selective permeable membrane for i, the chemical potential of i in the system must be identical to the measurable chemical potential μ_i itself. However, the system has its own chemical reactions, so the amount of chemical i in the system need not (algebraically) increase by dN_i mole.

19.5 Chemical equilibrium condition

Suppose the chemical composition of the system before adding dN_i is $\tilde{\boldsymbol{N}}$. Addition of dN_i changes the chemical composition of the system. Let this change be $d\tilde{\boldsymbol{N}} = \{d\tilde{N}_i\}$. The required Gibbs energy for this change (under constant T and P) is

$$\sum_j \mu_j d\tilde{N}_j. \tag{19.10}$$

Quasistatic and reversible addition of dN_i requires the Gibbs energy change of $\mu_i dN_i$. Therefore, these two must be identical:

$$\mu_i dN_i = \sum_j \mu_j d\tilde{N}_j. \tag{19.11}$$

In general, the following equality must hold:

$$\boldsymbol{\mu} \cdot d\boldsymbol{N} = \boldsymbol{\mu} \cdot d\tilde{\boldsymbol{N}}. \tag{19.12}$$

In particular, for a closed system

$$0 = \boldsymbol{\mu} \cdot d\tilde{\boldsymbol{N}} \tag{19.13}$$

must hold even if there are chemical reactions.[290] This is the chemical equilibrium condition for a closed system. In this section, however, we will consider the cases without any chemical reactions (the reactions will be considered in Section 25).

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[290] This is why the Gibbs relation does not have any chemical potential, if the system is closed (as correctly pointed out in Kirkwood and Oppenheim).

19.6 'Chemical work' minimization principle

In many chemical experiments, systems have no work exchange except for the volume work. Since

$$dG = -SdT + VdP + \sum_i \mu_i dN_i, \tag{19.14}$$

$dG = dZ$ (→**17.1**) under constant temperature and pressure conditions; materials exchanges only change the Gibbs energy. Under reversible and quasistatic conditions, we have

$$\Delta G = Z. \tag{19.15}$$

Then, what happens if the process is not reversible? Since $G = A + PV$, if W consists only of volume work, then

$$\Delta G = \Delta A - W = \Delta A + P\Delta V, \tag{19.16}$$

However, the (extended) minimum work principle (18.8) implies

$$\Delta G \leq Z. \tag{19.17}$$

This inequality may be called the minimum chemical work principle.

In electrochemistry this principle gives the minimum electric energy required to charge an electric cell. Also, exactly the same logic used in deriving the maximum work principle (18.7) implies

$$|\Delta G| \geq |Z|. \tag{19.18}$$

That is, the electric energy taken out from a cell is maximum if the process is reversible. Thus, this should be called the maximum chemical work principle.

19.7 Principle of Gibbs energy minimization

If a closed system does not exchange work other than volume work, (19.17) holding under constant temperature and pressure conditions becomes

$$\Delta G \leq 0. \tag{19.19}$$

That is, if a change can actually occur under constant temperature and pressure without any external net contribution of operational coordinate change except for the volume coordinate, the Gibbs energy should decrease.

This implies that the intial state of the system was actually not an equilibrium state, so under constant temperature and pressure, if the system is in equilibrium, any variation of the state without exchanging materials and work other than volume work implies

$$\Delta G \geq 0 \tag{19.20}$$

must hold for any thermodynamic variation under constant T and P. Thst is, just as **12.6**, but defined as follows with the constant T and P condition: For a function $J(T,P,\boldsymbol{Y}')$ of T, P and operational coordinates except for V denoted as $\boldsymbol{Y}'$,

$$\Delta J(T,P,\boldsymbol{Y}') = \sum_{i\in\mathcal{P}} J(T,P,\boldsymbol{Y}'_i) - J(T,P,\boldsymbol{Y}'), \tag{19.21}$$

where $\mathcal{P}$ denotes the set of subsytems by a particular partition of the original system into subsystems, and $\boldsymbol{Y}' = \sum_{i\in\mathcal{P}} \boldsymbol{Y}'_i$.[291] For any equilibrium state under constant temperature and pressure (19.20) must hold. This is called the *Gibbs energy minimization principle*, which is a global principle for a state to be in equilibrium. (19.20) is just a Jensen's inequality, because G under constant T and P is a convex function of $\boldsymbol{Y}'$, simply because so is E (→**13.9**).

19.8 Phase equilibrium under constant temperature and pressure

When two distinct phases[292] of a pure substance coexist (as ice floating in water), we can interpret the two phases A and B in contact through an interface as two systems A and B in contact through a wall that allows free exchange of matter, heat and volume. The condition that these two systems are in equilibrium under constant T and P is the principle of Gibbs energy minimization (→**19.7**). The Gibbs energy of the total system is the sum of the Gibbs energies of A and B. Thus, if there is only one chemical substance (or without any chemical reaction), the chemical component is identical to the materials coordinate, so the minimization principle gives:

$$G_{\mathrm{A+B}}(T,P,N) = \min N'[G_{\mathrm{A}}(T,P,N-N') + G_{\mathrm{B}}(T,P,N')]. \tag{19.22}$$

Differentiating this with respect to N', we get

$$-\mu_{\mathrm{A}} + \mu_{\mathrm{B}} = 0. \tag{19.23}$$

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[291] Here, we consider only simple systems, but generalizing our discussion to compound systems is just as discussed before in **12.6** .

[292] For a precise definition of 'phase,' see **23.2**.

That is, the chemical potentials must be the same between the two phases in equilibrium.

19.9 Clapeyron-Clausius equation

Understanding how the boiling point changes as pressure changes is a practically important question (recall the vacuum distillation). To this end, we need to know how the chemical potential changes as a function of pressure. If the system has the volume as the only work coordinate, then (17.11) becomes

$$d\mu = vdP - sdT, \tag{19.24}$$

where v is the molar volume $v = V/N$ and s is the molar entropy $s = S/N$.

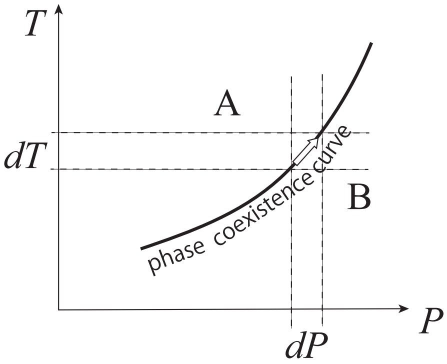

Figure 19.1: How does the coexistence temperature change, when the pressure is changed along the coexistence curve? We wish to know the slope of the white arrow.

Let Δ denote the change due to the transition A→B. Take dT and dP along the white arrow in Fig. 19.1. $\Delta\mu = 0$ becomes

$$\Delta v\, dP = \Delta s\, dT, \tag{19.25}$$

where $\Delta v = v_{\mathrm{B}} - v_{\mathrm{A}}$ and $\Delta s = s_{\mathrm{B}} - s_{\mathrm{A}}$. dT/dP is the slope of the white arrow:

$$\left.\frac{dP}{dT}\right|_{\text{coexistence}} = \frac{s_{\mathrm{B}} - s_{\mathrm{A}}}{v_{\mathrm{B}} - v_{\mathrm{A}}}. \tag{19.26}$$

This is called the *Clapeyron-Clausius equation*. If we write the latent heat of A→B as L, the relation between the latent heat and Δs is given by (17.35), so (19.26) becomes

$$\left.\frac{dP}{dT}\right|_{\text{coexistence}} = \frac{L}{T\Delta v}. \tag{19.27}$$

Vapor pressure is the pressure exerted by a vapor in equilibrium with its condensed phases (solid or liquid) at a given temperature T in a closed system. Thus, if phase B is a condensed phase (liquid or solid), and if A is a gas phase in the above, P is the vapor pressure of this substance at temperature T.

19.10 Ideal dilute mixture

In **17.14**, we considered an ideal liquid mixture of any proportion based on two empirical laws, Dalton's law of partial pressures and Raoult's law. Dalton's law may be more reliable than Raoult's law, which is not so reliable for real liquids of comparable component ratios. However, if the mole fraction x is sufficiently close to 0 or 1, Raoult's law is fairly accurate. Therefore, the chemical potential formulas for the ideal liquid mixtures (17.28) and (17.29) are fairly reliable for small x. If this is the case, the mixture is called an *ideal dilute mixture*.

If a gas dissolves with only a small amount in a certain liquid, the mole fraction x of the gas in the liquid is proportional to the gas pressure, known as *Henry's law*. This law is closely related to Raoult's law if we accept Dalton's law, but much more reliable than Raoult's law.

19.11 Melting point depression

Suppose material A is desolved in liquid B with a small mole fraction x. The chemical potential of B at temperature T (P is not varied, so it is not written) reads (see (17.29))

$$\mu_L(T) = \mu_L^{\ominus}(T) + RT\log(1-x). \tag{19.28}$$

Here, $\mu_L^{\ominus}(T)$ is the chemical potential of pure liquid B.[293] If the mixture is cooled sufficiently, crystals (i.e., the solid phase) of almost pure B will separate out. At the melting point T_m of pure B, if we write the chemical potential of pure solid B as $\mu_S^{\ominus}(T)$, then, as we have already seen in **19.8**,

$$\mu_L^{\ominus}(T_m) = \mu_S^{\ominus}(T_m). \tag{19.29}$$

If an impurity mixes with a melt, its freezing point goes down: $T_m \to T_m - \Delta T$. In this situation the pure crystal is in equilibrium with the impurity-containing liquid B whose chemical potential is (19.28). Thus, the equilibrium condition is

$$\mu_S^{\ominus}(T_m - \Delta T) = \mu_L^{\ominus}(T_m - \Delta T) + R(T_m - \Delta T)\log(1-x). \tag{19.30}$$

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[293] Throughout this section $\ominus$ implies quantities for pure substances.

Assume x is small. Taylor expanding this formula in x (note that $\Delta T = O[x]$), we obtain

$$\frac{\partial}{\partial T_m}[\mu_S^\ominus(T_m) - \mu_L^\ominus(T_m)]\Delta T = RT_m x. \tag{19.31}$$

The partial derivative of μ is computed according to (17.11), so we get

$$[s_L(T_m) - s_S(T_m)]\Delta T = \frac{L}{T_m}\Delta T = RT_m x, \tag{19.32}$$

where L is the melting heat. From this the extent of the *melting point depression* is given by

$$\Delta T = \frac{RT_m^2}{L}x. \tag{19.33}$$

Even if we dissolve x mol of a solute, its 'molecule' might separate into several pieces to increase the effective molarity of the solute. This results in the melting point depression larger than the expected value (19.33). This observation is historically important, because it gave an evidence for ionization of electrolytes.

19.12 Boiling point elevation

If material A that hardly vaporizes is dissolved in a liquid, its boiling point T_b increases by ΔT. At this elevated boiling point the pure vapor of the liquid and the liquid containing A by x mole fraction are in equilibrium. Therefore, the formula corresponding to (19.30) reads

$$\mu_G^\ominus(T_b + \Delta T) = \mu_L^\ominus(T_b + \Delta T) + R(T_b + \Delta T)\log(1 - x). \tag{19.34}$$

Using a similar logic leading to **19.11**, we obtain the *boiling point elevation*

$$\Delta T = \frac{RT_b^2}{L}x, \tag{19.35}$$

where L is the evaporation heat of the pure liquid.

The reason why the boiling point increases due to the impurity from T_b is that its vapor pressure at T_b is not P but is reduced by ΔP. To estimate this amount we have only to write down the agreement of the chemical potentials at T_b under pressure $P - \Delta P$:

$$\mu_G^\ominus(T_b, P - \Delta P) = \mu_L^\ominus(T_b, P - \Delta P) + RT_b\log(1 - x). \tag{19.36}$$

We need the pressure dependence of the chemical potential that may be obtained from (19.24). Taylor-expanding the equality around P, we get

$$-v_G \Delta P = -v_L \Delta P - RT_b x. \tag{19.37}$$

In the present case the molar volume v_G of the gas is overwhelmingly larger than that of the liquid v_L, so we may ignore v_L. Furthermore, the gas can be approximated as an ideal gas, so we may use $v_G = RT/P$. Thus, we get

$$\Delta P = Px. \tag{19.38}$$

19.13 Osmotic pressure: van't Hoff's law

Suppose there is a pure solvent and a solution consisting of the solvent and a solute in contact through a selective membrane that only allows the solvent to go through. Since the chemical potential of the solvent is smaller in the solution than in the pure solvent as seen in (19.28), the solvent pushes into the solution. To prevent this influx, we must apply pressure on the solution side. The minimum pressure π required to prevent this influx is called the *osmotic pressure* (Fig. 19.2).

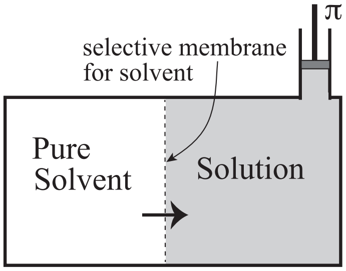

Figure 19.2: The horizontal arrow indicates the tendency for solvent to invade.

If the pressure of the solvent is P, the solution must be maintained at pressure $P+\pi$ to prevent any flow. The equilibrium condition for the solvent reads

$$\mu^{\ominus}{}_{\text{solv}}(P+\pi, T) + RT\log(1-x) = \mu^{\ominus}{}_{\text{solv}}(P, T). \tag{19.39}$$

By the Taylor expansion, just as (19.30), we get *van't Hoff's law*:

$$-v\pi = -RTx \ \Rightarrow \ \pi = nRT, \tag{19.40}$$

where n is the molarity of the solute: since x is a molar fraction, and $x \ll 1$, x is almost identical to the solute moles per one mole of the solvent, whose volume is v, so the molarity n of the solute is given by $n = x/v$.

19.14 The colligative properties

Raoult's law (→**17.13**), Henry's law (→**19.10**), melting point depression(→**19.11**), boiling point elevation (→**19.12**) and van't Hoff's law (→**19.13**) are all independent of the peculiarities of individual substances and all due to the terms $\log x$ or $\log(1-x)$ in the chemical potential (that is, due to the mole fraction), so they can be understood in a unified fashion (or all at once as a bunch). Therefore, they are called the *colligative properties.*[294]

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[294] colligative ⇐ co + ligate = tying up together.

20 Making full use of Jacobians

20.1 Strong differentiability of internal energy: a review

Internal energy is a strongly differentiable convex function of entropy S, work coordinates $\boldsymbol{X}$ and materials coordinates $\boldsymbol{N}$. Therefore,

$$dE = TdS + \sum x_i dX_i + \sum \mu_i dN_i \tag{20.1}$$

is an exact form. From the convexity of E, the intensive conjugate variables, T, x_i and μ_i are (Lipshitz) continuous functions of thermodynamic coordinates. However, the thermodynamic principles cannot show greater smoothness, such as the differentiability of T, from its principles.

Empirically, as long as there is no phase transition, fairly high-order partial differentiability seems to hold. Therefore, let us assume that the internal energy is a C^2 function of the thermodynamic coordinates in this section.[295]

Those who feel uneasy about the notation of partial derivatives in thermodynamics should read **9.2**.

20.2 Legendre-Fenchel transformation and changing independent variables

The independent variables of complete thermodynamic functions obtained from E by Legendre-Fenchel transformation (→**18.6**) are not necessarily extensive quantities. Therefore, if the dimension of the thermodynamic space of a system is $\mathcal{D}$, we encounter situations requiring a set of $\mathcal{D}$ thermodynamic variables to be replaced by another set of $\mathcal{D}$ thermodynamic variables. For example, the independent variables of the Gibbs energy are $T, P, \boldsymbol{X} \setminus V$ and $\boldsymbol{N}$, so it is required to express this set in terms of $S, \boldsymbol{X}, \boldsymbol{N}$ to use the fundamental equation (→**11.12**). We have already differentiated chemical potentials with respect to T, for example.

Thus, to determine the outcome of twice differentiability of internal energy, it is

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[295] Equilibrium statistical mechanics can demonstrate that E is C^ω if there is no phase transitions (rather, phase transitions are defined as the states where the C^ω-nature of free energy is lost). Remember that this is only a model result; not empirical at all. However, we should clearly recognize that the statistical mechanics framework is a consequence of thermodynamics, if we accept the typicality argument of the microstates. Thus, statistical mechanics is so good a model of thermodynamics that one may wish to regard it more basic than thermodynamics under the prejudice that smaller scales are closer to the fundamental.

convenient to be able to compute freely the results of the derivatives of any thermodynamic variable with respect to another thermodynamic variable.

20.3 Chain rule

Let us differentiate an n variable function $f(\boldsymbol{X})$ of variables $X_1, \cdots, X_n$ (collectively denoted as $\boldsymbol{X}$) with another set of n variables $x_1, \cdots, x_n$ (collectively denoted as $\boldsymbol{x}$).[296]

Remark From this unit to unit **20.6** X and x are not work coordinates and their conjugates but general variables. Uppercase (resp., Lowercase) letters need not mean extensive (resp. intensive) variables.

Here, we assume that the transformation $\boldsymbol{X} \to \boldsymbol{x}$ is diffeomorphic.[297] The following formal calculations are reliable as long as the smooth map $\boldsymbol{X} \to \boldsymbol{x}$ is bijective.

Let us assume that f be a function of $\boldsymbol{x}$, and apply the chain rule:

$$\left(\frac{\partial f}{\partial x_i}\right)_{x_i^c} = \sum_{j=1}^{n} \left(\frac{\partial X_j}{\partial x_i}\right)_{x_i^c} \left(\frac{\partial f}{\partial X_j}\right)_{X_j^c}. \tag{20.2}$$

Here, the superscript c means that from the relevant set of variables we remove the one with this mark. If we define a column vector

$$\frac{\partial}{\partial \boldsymbol{X}} = \left(\left(\frac{\partial}{\partial X_1}\right)_{X_1^c}, \cdots, \left(\frac{\partial}{\partial X_n}\right)_{X_n^c}\right)^t, \tag{20.3}$$

etc., where superscript t implies the transposition, (20.2) can be succinctly expressed as

$$\frac{\partial f}{\partial \boldsymbol{x}} = \left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right] \frac{\partial f}{\partial \boldsymbol{X}}. \tag{20.4}$$

Here, the following $n \times n$ matrix is used:

$$\left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right] = \mathrm{matr}\left(\left(\frac{\partial X_j}{\partial x_i}\right)_{x_i^c}\right) \tag{20.5}$$

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[296] In the rest of this section $\boldsymbol{X}$ and $\boldsymbol{x}$ denote general variables and not the work coordinates and their conjugate variables.

[297] One to one and differentiable in both ways; More intuitively, a map that is 'smooth' and that maps any sufficiently small cube around each point $\boldsymbol{X}$ to another nondegenerate n-dimensional shape around its image $\boldsymbol{x}$; the map linearized at any point becomes a regular, i.e., invertible, linear map.

$$= \begin{pmatrix} \left(\frac{\partial X_1}{\partial x_1}\right)_{x_1^c} & \left(\frac{\partial X_2}{\partial x_1}\right)_{x_1^c} & \left(\frac{\partial X_3}{\partial x_1}\right)_{x_1^c} & \cdots & \left(\frac{\partial X_n}{\partial x_1}\right)_{x_1^c} \\ \left(\frac{\partial X_1}{\partial x_2}\right)_{x_2^c} & \left(\frac{\partial X_2}{\partial x_2}\right)_{x_2^c} & \ddots & \cdots & \left(\frac{\partial X_n}{\partial x_2}\right)_{x_2^c} \\ \left(\frac{\partial X_1}{\partial x_3}\right)_{x_3^c} & \ddots & \ddots & \ddots & \left(\frac{\partial X_n}{\partial x_3}\right)_{x_3^c} \\ \vdots & \vdots & \ddots & \ddots & \vdots \\ \left(\frac{\partial X_1}{\partial x_n}\right)_{x_n^c} & \left(\frac{\partial X_2}{\partial x_n}\right)_{x_n^c} & \cdots & \cdots & \left(\frac{\partial X_n}{\partial x_n}\right)_{x_n^c} \end{pmatrix}. \tag{20.6}$$

If we further apply a diffeomorphism from $\boldsymbol{x}$ to n variables $a_1, \cdots, a_n$ (collectively denoted as $\boldsymbol{a}$), we can write

$$\frac{\partial f}{\partial \boldsymbol{a}} = \left[\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{a}}\right] \left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right] \frac{\partial f}{\partial \boldsymbol{X}}, \tag{20.7}$$

and the variable changes may be written in terms of the matrix multiplication:

$$\left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{a}}\right] = \left[\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{a}}\right] \left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right]. \tag{20.8}$$

You should explicitly write the two-variable case to confirm the relation.

20.4 Jacobian

The determinant of the matrix introduced in (20.6), which is called the Jacobi matrix, is known as the *Jacobian.* We use the following notation:

$$\frac{\partial(X_1, \cdots, X_n)}{\partial(x_1, \cdots, x_n)} = \frac{\partial(\boldsymbol{X})}{\partial(\boldsymbol{x})} = \det\left(\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right) = \det\left(\left(\frac{\partial X_j}{\partial x_i}\right)_{x_i^c}\right). \tag{20.9}$$

In this notation, the variables upstairs represent dependent variables and the variables downstairs represent independent variables.

In particular, if we have only two variables

$$\frac{\partial(X, Y)}{\partial(x, y)} = \begin{vmatrix} \left(\frac{\partial X}{\partial x}\right)_y & \left(\frac{\partial Y}{\partial x}\right)_y \\ \left(\frac{\partial X}{\partial y}\right)_x & \left(\frac{\partial Y}{\partial y}\right)_x \end{vmatrix} = \left(\frac{\partial X}{\partial x}\right)_y \left(\frac{\partial Y}{\partial y}\right)_x - \left(\frac{\partial X}{\partial y}\right)_x \left(\frac{\partial Y}{\partial x}\right)_y. \tag{20.10}$$

20.5 Computational rules due to Jacobians being determinants

To take advantage of the Jacobian formulation of partial derivatives, we only need to memorize a few simple rules (as summarized in **20.12**), some of which are direct consequences of Jacobians being determinants.

If we exchange two columns or two rows, a determinant switches its sign. From its definition (20.9), if we change the orders of two dependent or independent variables, the Jacobian switches its sign. In particular, for the two variable case we can explicitly write

$$\frac{\partial(X,Y)}{\partial(x,y)} = -\frac{\partial(Y,X)}{\partial(x,y)} = \frac{\partial(Y,X)}{\partial(y,x)} = -\frac{\partial(X,Y)}{\partial(y,x)}. \tag{20.11}$$

If we multiply a constant b to a column or row of a determinant, the determinant itself is multiplied by b. We only need the case where $b = -1$. In particular, for the two variable case we can explicitly write

$$\frac{\partial(-X,Y)}{\partial(x,y)} = \frac{\partial(X,-Y)}{\partial(x,y)} = \frac{\partial(X,Y)}{\partial(-x,y)} = \frac{\partial(X,Y)}{\partial(x,-y)} = -\frac{\partial(X,Y)}{\partial(x,y)}. \tag{20.12}$$

20.6 The chain rule in terms of Jacobians

The determinant of (20.8) reads

$$\frac{\partial(X_1,\cdots,X_n)}{\partial(a_1,\cdots,a_n)} = \frac{\partial(x_1,\cdots,x_n)}{\partial(a_1,\cdots,a_n)}\frac{\partial(X_1,\cdots,X_n)}{\partial(x_1,\cdots,x_n)}. \tag{20.13}$$

Determinants are just numbers, so we can exchange the order of multiplication to write

$$\frac{\partial(X_1,\cdots,X_n)}{\partial(a_1,\cdots,a_n)} = \frac{\partial(X_1,\cdots,X_n)}{\partial(x_1,\cdots,x_n)}\frac{\partial(x_1,\cdots,x_n)}{\partial(a_1,\cdots,a_n)}. \tag{20.14}$$

Notice that this implies an algebraic rule: if we have the same factors in the numerator and the denominator, we can cancel them. In the calculation utilizing Jacobians, differential calculus turns into algebra. In thermodynamics such a formal calculation invariably gives correct results.

In the two-variable case, this formal calculation rule may be illustrated as follows. First, separate the two factors in the upstairs and downstairs (the numerator and the denominator), and then throw in identical factors in the open slots:

$$\frac{\partial(X,Y)}{\partial(x,y)} = \frac{\partial(X,Y)}{}\frac{}{\partial(x,y)} = \frac{\partial(X,Y)}{\partial(A,B)}\frac{\partial(A,B)}{\partial(x,y)}. \tag{20.15}$$

Here, A and B may be anything that can be used as a set of independent variables. That is, (A,B) are at least locally diffeomorphic to (X,Y) and to (x,y).

20.7 Partial derivatives in terms of Jacobians

In the Jacobian expression, the variables downstairs are independent variables for a function F of $\boldsymbol{x}$

$$\frac{\partial(F, x_2 \cdots, x_n)}{\partial(x_1, x_2, \cdots, x_n)} = \det \begin{pmatrix} \left(\frac{\partial F}{\partial x_1}\right)_{x_1^c} & 0 & 0 & 0 & \cdots & 0 & 0 \\ \left(\frac{\partial F}{\partial x_2}\right)_{x_2^c} & 1 & 0 & 0 & \cdots & 0 & 0 \\ \left(\frac{\partial F}{\partial x_3}\right)_{x_3^c} & 0 & 1 & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & 0 & 1 & \ddots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ \left(\frac{\partial F}{\partial x_n}\right)_{x_n^c} & 0 & 0 & \cdots & \cdots & 0 & 1 \end{pmatrix} = \left(\frac{\partial F}{\partial x_1}\right)_{x_1^c}. \tag{20.16}$$

In particular, for the two-variable case

$$\frac{\partial(F, y)}{\partial(x, y)} = \det \begin{pmatrix} \left(\frac{\partial F}{\partial x}\right)_y & 0 \\ \left(\frac{\partial F}{\partial y}\right)_x & 1 \end{pmatrix} = \left(\frac{\partial F}{\partial x}\right)_y. \tag{20.17}$$

Even for cases with many variables, if we wish to consider only two variables among them, we may manipulate the formulas as if there are no other variables, as can be guessed from the structure of the matrix in (20.16).

20.8 Basic relations obtained from the chain rule

Let X and Y be thermodynamic variables. Then, trivially,

$$\frac{\partial(X, Y)}{\partial(X, Y)} = 1. \tag{20.18}$$

If we apply (20.15) to this formula, we obtain

$$1 = \frac{\partial(X, Y)}{\partial(X, Y)} = \frac{\partial(X, Y)}{\partial(A, B)} \frac{\partial(A, B)}{\partial(X, Y)}. \tag{20.19}$$

That is,

$$\frac{\partial(X, Y)}{\partial(A, B)} = 1 \Bigg/ \frac{\partial(A, B)}{\partial(X, Y)}. \tag{20.20}$$

Combining this formula and the partial derivatives expressed in terms of Jacobians (→**20.7**), for example, we obtain

$$\frac{\partial(X,Y)}{\partial(x,Y)} = 1 \Bigg/ \frac{\partial(x,Y)}{\partial(X,Y)} \ \Rightarrow\ \left(\frac{\partial X}{\partial x}\right)_Y = 1 \Bigg/ \left(\frac{\partial x}{\partial X}\right)_Y . \tag{20.21}$$

Although this relation may appear trivial from an algebraic point of view, analytically, it is not so trivial. On the left-hand side, both X and Y are regarded as functions of x and $Y(x,y)$, and the derivative is with respect to x with $Y(x,y)$ being fixed. On the right-hand side both x and y are regarded as functions of X and Y and the derivative is with respect to X with Y being fixed. An example of this is (for specific heats →**14.6**)

$$\left(\frac{\partial T}{\partial S}\right)_V = 1 \Bigg/ \left(\frac{\partial S}{\partial T}\right)_V = \frac{T}{C_V}. \tag{20.22}$$

Since algebraic calculations are allowed, we can perform, for example,

$$\frac{\partial(x,X)}{\partial(y,X)} = \frac{\partial(x,X)}{} \Bigg/ \frac{\partial(y,X)}{} = \frac{\partial(x,X)}{\partial(y,x)} \Bigg/ \frac{\partial(y,X)}{\partial(y,x)} = -\frac{\partial(X,x)}{\partial(y,x)} \Bigg/ \frac{\partial(X,y)}{\partial(x,y)} . \tag{20.23}$$

In terms of partial derivatives, this reads

$$\left(\frac{\partial x}{\partial y}\right)_X = -\left(\frac{\partial X}{\partial y}\right)_x \Bigg/ \left(\frac{\partial X}{\partial x}\right)_y . \tag{20.24}$$

If we set $x = P$, $y = T$, $X = V$, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \Bigg/ \left(\frac{\partial V}{\partial P}\right)_T = \frac{\alpha}{\kappa}, \tag{20.25}$$

where α is the isobaric thermal expansion coefficient and κ is the isothermal compressibility:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T . \tag{20.26}$$

20.9 Young's theorem and Maxwell's relations

Young's theorem **9.7** states that if all the twice partial derivatives of E exist, their results do not depend on the order of differentiation. That is, if we use Y_i to represent, entropy, work coordinates or materials coordinates[298]

$$\frac{\partial^2 E}{\partial Y_i \partial Y_j} = \frac{\partial^2 E}{\partial Y_j \partial Y_i}. \tag{20.27}$$

That is,

$$\left(\frac{\partial y_i}{\partial Y_j}\right)_{Y_j^c} = \left(\frac{\partial y_j}{\partial Y_i}\right)_{Y_i^c}. \tag{20.28}$$

This relation is called *Maxwell's relations* in thermodynamics. For example, for a gas with only volume as its work coordinate

$$dE = TdS - PdV \tag{20.29}$$

yields the following Maxwell's relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V. \tag{20.30}$$

Physically, this is remarkable; it quantitatively relates the temperature change due to a volume change under adiabatic conditions to the pressure change when entropy is changed (i.e., heat is added) under constant volume. It should be hard to understand the relation intuitively.[299]

20.10 Unified Maxwell's relation in terms of Jacobians

Maxwell's relations hold not only for internal energy, but for any sufficiently smooth twice differentiable quantities. Therefore, for example, for complete thermodynamic functions there are many Maxwell's relations. However, the only formula that needs to be memorized is the following:

$$\frac{\partial(X, x)}{\partial(y, Y)} = 1. \tag{20.31}$$

Here, uppercase letters denote extensive quantities, and lowercase letters denote intensive quantities, and the alphabetical correspondence implies the conjugate relation: (X, x) denotes, for example, (S, T), $(V, -P)$, (N, μ), etc.

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[298] If we choose the conventional chemical coordinates (= chemical composition variables), then this is true only without any chemical reaction.

[299] Or, even by statistical mechanics alone.

This formula has been demonstrated in **9.18**.[300] An algebraic formal 'derivation' is in **20.11**.

20.11 Unification of Maxwell's relations: algebraic 'explanation'

Let us rewrite (20.28) as

$$\left(\frac{\partial x}{\partial Y}\right)_{X,\cdots} = \left(\frac{\partial y}{\partial X}\right)_{Y,\cdots}, \tag{20.32}$$

denoting with $\cdots$ the other extensive variables than X and Y. The essence of this equation is

$$\frac{\partial(x,X)}{\partial(Y,X)} = \frac{\partial(y,Y)}{\partial(X,Y)}. \tag{20.33}$$

Therefore,

$$\frac{\partial(x,X)}{\partial(y,Y)} = \frac{\partial(Y,X)}{\partial(X,Y)} = -1. \tag{20.34}$$

By combining this with (20.11), we immediately obtain (20.31). Needless to say, this is not a proof, but rather a mnemonic.

20.12 Summary of Jacobian technique

The definition of the Jacobian is provided in **20.4**, esp., (20.9). Thus, the partial derivative can be written as (→**20.7**)

$$\left(\frac{\partial A}{\partial B}\right)_{\cdots} = \frac{\partial(A,\cdots)}{\partial(B,\cdots)}. \tag{20.35}$$

All the calculations required when we use Jacobians are algebraic and are based only on the following three rules:
(i) The rule for signs (→**20.5**): horizontal exchange of letters[301] or changing the sign of a letter switches the sign:

$$\frac{\partial(X,Y)}{\partial(x,y)} = -\frac{\partial(Y,X)}{\partial(x,y)} = \frac{\partial(Y,X)}{\partial(y,x)} = -\frac{\partial(X,Y)}{\partial(y,x)}, \tag{20.36}$$

$$\text{for example, } \frac{\partial(-X,Y)}{\partial(x,y)} = -\frac{\partial(X,Y)}{\partial(x,y)}. \tag{20.37}$$

---

[300] To derive the formula considering its physical meaning is with poor taste, but thus derived

$$\frac{\partial(P,V)}{\partial(T,S)} = 1$$

is known for a long time.

[301] which may be called 'transposition.'

(ii) Chain rule (→**20.6**): The same factors $\partial(\cdots)$ may be inserted/removed:

$$\frac{\partial(X,Y)}{\partial(x,y)} = \frac{\partial(X,Y)}{}\frac{}{\partial(x,y)} = \frac{\partial(X,Y)}{\partial(A,B)}\frac{\partial(A,B)}{\partial(x,y)}. \tag{20.38}$$

(iii) Maxwell's relation (→**20.10**): for arbitrary conjugate pairs (X,x) and (Y,y)

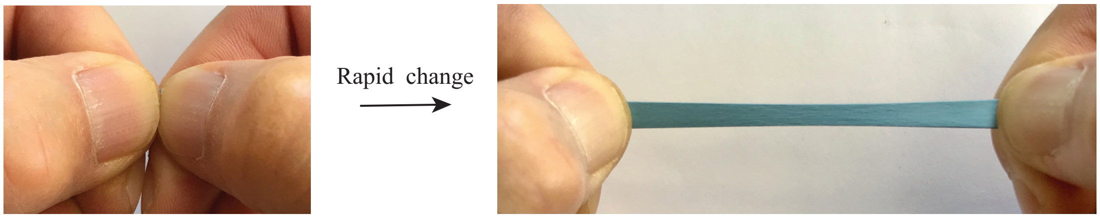
$$\frac{\partial(X,x)}{\partial(y,Y)} = 1. \tag{20.39}$$

Practice the usage of Jacobians through the examples in the next section.

21 Entropic elasticity

21.1 Experiments with a rubber band

Prepare a wide rubber band (for bundling broccoli and asparagus). As a temperature sensor use your lips. First, lightly touch the rubber band with your lips to confirm that it is at room temperature; it should feel somewhat cool. Next, as illustrated in the photo 21.1 Left, hold both ends of a very small portion of the band tightly between your thumbs and fingers, and quickly and strongly stretch it (Fig. 21.1 Right).



Hold firmly

Stretch at once

Figure 21.1: If we stretch a small portion of a wide rubber band quickly and strongly, we can approximately realize an adiabatic reversible quasistatic stretching of a rubber band.

Immediately after stretching, put the stretched portion to your lip. It should feel warm. Keep stretching strongly for a while to allow it to equilibrate roughly with the room temperature, and then suddenly stop stretching. The shrunk portion should now feel cool, which you can confirm by touching it with your lips.

Although we use the term "quickly" to describe the stretching process, the actual stretching speed is relatively slow compared to the relaxation rate of the rubber polymers, resulting in a reversible quasistatic process. Furthermore, the heat flow from the ambient air and our hands during the stretching process is limited, allowing for an adequate adiabatic condition. In other words, we have approximately realized an adiabatic reversible and quasistatic stretching of the rubber band.

21.2 Summary of empirical observations about rubber bands

From the experiment in **21.1** and related ones, we can observe the following:

(1) An adiabatic and reversible quasistatic stretching increases the temperature of the stretched portion.

(2) Adiabatic and reversible quasistatic shrinking decreases the temperature of the

shrunk portion. This is just the reversal of (1), and is not surprising, but still a notable fact.
(3) If we suspend a weight with a rubber band and warm it, the weight is raised.
(4) To prevent the warming of the rubber band from raising the weight, we must increase the weight.
The effects of (3) and (4) are not large and are not as easily observed as (1) and (2).[302]

An obvious fact we must note is that increasing the length L of the rubber band requires a stretching force F and, consequently, we must do some work.

21.3 Thermodynamics of a rubber band

To develop the thermodynamics of any system, we must first set up its thermodynamic space. That is, we must choose its thermodynamic coordinates. To describe the state of a rubber band, we need its internal energy and the length L. When stretched, a rubber band becomes thinner, but it is empirically known that its volume is approximately constant, so, for example, its width is not an independent coordinate. Therefore, we adopt L as its work coordinate. The work required to change L with a stretching force F is expressed as $\omega = FdL$. Thus, the thermodynamic space of the rubber band is spanned by E and L, and the Gibbs relation is given by

$$dE = TdS + FdL. \tag{21.1}$$

The facts (1)-(4) in **21.2** are expressed as:

$$(1,2) \qquad \left(\frac{\partial T}{\partial L}\right)_S > 0. \tag{21.2}$$

$$(3) \qquad \left(\frac{\partial L}{\partial T}\right)_F < 0. \tag{21.3}$$

$$(4) \qquad \left(\frac{\partial F}{\partial T}\right)_L > 0. \tag{21.4}$$

For an adiabatic and reversible quasistatic process the entropy of the system remains constant, so $S =$ const. in (21.2) means the adiabatic condition.

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[302] According to Shixian Zhang, Quanling Yang & Qing Wang, Solid-state cooling by elastocaloric polymer with uniform chain-lengths Nature Commun. **13**, 9 (2022), an adiabatic temperature change of -15.3 K and an isothermal entropy change of 145 J kg^{-1}K^{-1} are obtained from poly(styrene-b-ethylene-co-butylene-b-styrene) near room temperature.

21.4 Mutual relations of empirical facts (1)-(4)

Are the empirical observations (1)-(4) in **21.3** independent? The most straightforward method for examining the relationships among these partial derivatives is to express them in terms of Jacobians (→**20.7**).

$$(1,2)\qquad \left(\frac{\partial T}{\partial L}\right)_S = \frac{\partial(T,S)}{\partial(L,S)} > 0. \tag{21.5}$$

$$(3)\qquad \left(\frac{\partial L}{\partial T}\right)_F = \frac{\partial(L,F)}{\partial(T,F)} < 0. \tag{21.6}$$

$$(4)\qquad \left(\frac{\partial F}{\partial T}\right)_L = \frac{\partial(F,L)}{\partial(T,L)} > 0. \tag{21.7}$$

Very often the presence of S in the formula is a nuisance. To eliminate S we can use a Maxwell's relation (→**20.10**)

$$\frac{\partial(T,S)}{\partial(L,F)} = 1 \tag{21.8}$$

or specific heats (→**14.6**). Let us first use the chain rule (20.38) and Maxwell's relation:

$$\frac{\partial(T,S)}{\partial(L,S)} = \frac{\partial(T,S)}{\qquad}\frac{\qquad}{\partial(L,S)} = \frac{\partial(T,S)}{\partial(L,F)}\frac{\partial(L,F)}{\partial(L,S)} = \frac{\partial(L,F)}{\partial(L,S)}. \tag{21.9}$$

S is still present, but its temperature dependence may be related to the heat capacity and is easy to measure (→**14.6**):

$$\frac{\partial(L,F)}{\partial(L,S)} = \frac{\partial(L,F)}{\qquad}\frac{\qquad}{\partial(L,S)} = \frac{\partial(L,F)}{\partial(L,T)}\frac{\partial(L,T)}{\partial(L,S)} = \left(\frac{\partial F}{\partial T}\right)_L \frac{T}{C_L}. \tag{21.10}$$

Here, C_L is the heat capacity of the rubber band under constant length. Thus, we arrive at

$$\left(\frac{\partial T}{\partial L}\right)_S = \left(\frac{\partial F}{\partial T}\right)_L \frac{T}{C_L}. \tag{21.11}$$

Since $C_L > 0$, and the positivity of the left-hand side was easy to observe (empirical fact (1) of **21.2**), this equation means (4).

(3) and (4) appear like two sides of a coin. To understand the relation, let us start with a single fact (say, (3)) and split its Jacobian expression as:

$$\left(\frac{\partial L}{\partial T}\right)_F = \frac{\partial(L,F)}{\partial(T,F)} = \frac{\partial(L,F)}{\qquad}\frac{\qquad}{\partial(T,F)}, \tag{21.12}$$

and then start thinking. Since (4) has the factor (T, L), let us introduce this: using the rule for the sign **20.12** (i), we get

$$\left(\frac{\partial L}{\partial T}\right)_F = \frac{\partial(L,F)}{\partial(T,L)}\frac{\partial(T,L)}{\partial(T,F)} = -\left(\frac{\partial F}{\partial T}\right)_L\left(\frac{\partial L}{\partial F}\right)_T \tag{21.13}$$

If we increase F, length L should increase, so the second partial derivative should be positive (this is an example of Le Chatelier's principle.→**22.8**). Therefore, (4) implies (3). That is, if we know (1) the rest may be obtained by thermodynamics.

In this unit, that $C_L > 0$ and that $(\partial F/\partial L)_T > 0$ are taken for granted; if these signs were opposite, horrible things would happen. For example, if the heat capacity were negative, the injecting heat into such a system would reduce its temperature, making it easier to absorb more heat. This would create something like a heat black hole. These signs are determined by the fundamental constraint resulting from the stability of the world, which we will discuss in the next section.

21.5 How does entropy change?

What happens to the entropy of a rubber band when it is stretched under a constant temperature? Equivalently, what is the sign of the following partial derivative? According to our experimental result

$$\left(\frac{\partial S}{\partial L}\right)_T = \frac{\partial(S,T)}{\partial(L,T)} = \frac{\partial(S,T)}{\partial(F,L)}\frac{\partial(F,L)}{\partial(L,T)} = -\frac{\partial(F,L)}{\partial(T,L)} = -\left(\frac{\partial F}{\partial T}\right)_L < 0. \tag{21.14}$$

That is, as long as the temperature is constant, entropy decreases as the band is stretched.

Entropy is not so easy to reduce (→**12.7**); the above inequality tells us that the reason why a rubber band resists being stretched is due to the entropy decrease. Such elasticity is called the *entropic elasticity*; The experimental fact (4) that increasing temperature 'strengthens' the rubber band is its characteristic.[303]

According to **17.16**, entropy is related to the amount of knowledge we need to describe a macro state in a detailed fashion. Following this point of view, (21.14) implies that stretching makes the description of polymers making the rubber band

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[303] **⟪Energetic elasticity⟫** The concept in contrast to entropic elasticity is *energetic elasticity*. This is due to the increase of energy by stretching and we encounter often with ordinary metal springs. Under a constant temperature, its E must increase with L. The ideal rubber band **21.6** is significantly different from this behavior.

simpler. Its exaggerated illustration is Fig. 21.2. That is, if stretched, the chains are more constrained and the shapes become simpler.

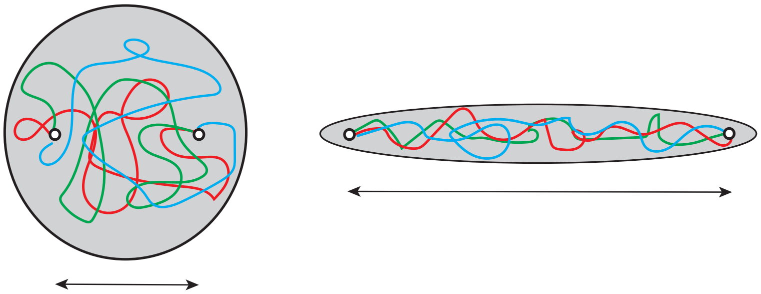

Figure 21.2: If stretched, the range where the chains can wiggle is restricted. Three different conformations are illustrated. The gray zone indicates the rough range where the chains can wiggle.

Then, what happens to the entropy if the rubber band length is kept constant, while increasing the stretching force? If we rely on the intuitive picture Fig. 21.2, the stretching force cannot be increased (or the spring constant cannot be increased) unless somehow entropy must be increased. Can we show this? That is,

$$\left(\frac{\partial S}{\partial F}\right)_L > 0\ ? \tag{21.15}$$

We always follow the same strategy:

$$\left(\frac{\partial S}{\partial F}\right)_L = \frac{\partial(S,L)}{\partial(F,L)} = \frac{\partial(S,L)}{\partial(T,L)}\frac{\partial(T,L)}{\partial(F,L)} = \frac{C_L}{T} \Big/ \left(\frac{\partial F}{\partial T}\right)_L > 0 \tag{21.16}$$

The inequality is due to (4) of **21.3**.

21.6 Ideal rubber band

Up to this point no internal energy has been mentioned. The actual rubber band becomes brittle if the temperature is too low, and melt if it is too high, indicating internal energy is crucial. However, around room temperature, E does not significantly depend on L. This is just as the ideal gas internal energy does not depend on volume (work coordinate). Therefore, the rubber band whose E does not depend on L is called an *ideal rubber band*. Just as the entropy of the ideal gas (i.e., the fundamental equation of the ideal gas (11.26)) can be written as a sum of the part dependent on E and that dependent on V, the entropy of the ideal rubber band can be written as the sum of the E-dependent part and the L-dependent part:

$$S(E,L) = S_e(E) + S_c(L). \tag{21.17}$$

Here, S_e is the energy depending portion and is independent of the stretching of the rubber bad. S_c is the portion dependent on the stretching. The temperature T is determined by the derivative of S_e. The adiabatic free shrinking should maintain E, so the temperature should not change. Isn't this contradictory to the experimental fact (2) of **21.2**? When the rubber band shrinks, it is impossible to make the force everywhere zero instantaneously, and also the relaxation time is very short, so even if we instantaneously releases the rubber band, free shrinking never happens, and only quasistatic change can be realized.

21.7 The principle of adiabatic cooling

If we allow a strongly stretched rubber band to relax at room temperature (adiabatic relaxation), the rubber band cools down as we have already experienced (**21.1** (2)): since

$$\left(\frac{\partial T}{\partial L}\right)_S > 0, \tag{21.18}$$

if we reduce L under constant S, T must decrease. This is the principle of *adiabatic cooling* (see Fig. 21.3).

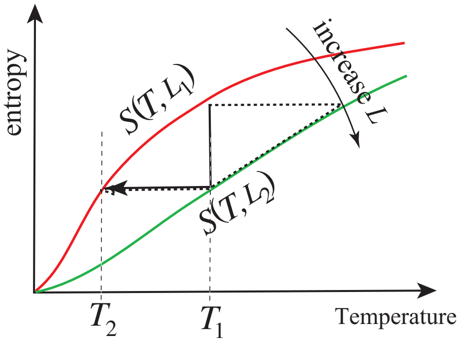

Figure 21.3: Initially, the system temperature is T_1. Under constant temperature, we increase L: $L_1 \to L_2$. This reduces the system entropy. Next, we return L to the original length adiabatically and reversibly. The entropy remains constant, so the system temperature goes down to T_2. The dotted curve denotes the process that occurs when the rubber band is stretched rapidly (i.e., adiabatically).

Unfortunately, we cannot use a rubber band to reduce the system temperature sufficiently, because (21.17) does not hold at low temperatures and the band becomes brittle. In actual low temperature physics experiments, dilute paramagnetic systems are used (→**21.8**).

21.8 Dilute paramagnets or ideal magnets: adiabatic demagnetization

The thermodynamic space of a magnet is spanned by the internal energy and magnetization M. Therefore, its Gibbs relation is given by (→**B.2**)

$$dE = TdS + BdM. \tag{21.19}$$

Here, for an ideal paramagnetic material, just as the ideal gas and idea rubber band, the following fundamental equation holds:

$$S = S_e(E) + S_c(M). \tag{21.20}$$

If an external magnetic field B is imposed, the magnetization aligns to the magnetic field direction. Therefore, there is a very good analogy to the stretching of a rubber band with a stretching force. That is,

$$\left(\frac{\partial T}{\partial B}\right)_S > 0 \tag{21.21}$$

holds. Therefore, if B is adiabatically reduced (*adiabatic demagnetization*), the system temperature goes down. The principle is understandable by replacing L with B in Fig. 21.3.

22 Stability of equilibrium states implied by convexity

Here, we discuss the stability of equilibrium states of a system in general. The stability of chemical equilibria specifically will be discussed in Section 24.

22.1 General remark on thermodynamic stability analysis

To study the stability of a state of a system, we apply a (small) perturbation to the system to examine the fate of the resulting perturbed equilibrium state. Since thermodynamics only deals with equilibrium states, the eventually obtained equilibrium state by the perturbation is understood as the resulting perturbed state, which is compared with the original unperturbed state. This means we study the outcomes of (small) thermodynamic variations (→**12.6**) applied to the system.

It goes without saying that the change of thermodynamic variables by a perturbation is obtained thermodynamically, since the resultant perturbed state is an equilibrium state.

As you will learn soon, we do not pursue stability per se in the perturbational analysis, but we only seek for the outcome of convexity of negative entropy $-S$ or internal energy E. Basically, Jensen's inequality (→**13.3**) gives the stability condition for equilibrium systems.

22.2 Stability of equilibrium states of an isolated system due to convexity[304]

For an isolated system, if it is a simple system, then the convexity of $-S$ implies that for any thermodynamic variation = (→**12.6**)

$$\Delta S \leq 0. \tag{22.1}$$

If the system is a compound system, and allowed thermodynamics variations never alters the internal constraints, then we have the same inequality as above. However, if thermodynamic variation does not respect the internal constraints, there can be some variation satisfying

$$\Delta S > 0. \tag{22.2}$$

---

[304] This is a repetition of **12.7**.

This implies that for the compound system under study, a certain relaxing of its internal constraints spontaneously alter its equillibrium state. Therefore, (22.2) is called the *evolution criterion* for the equilibrium system when internal constraints are relaxed.

Traditionally, (22.1) is called the stability condition of the equilibrium system, but it is nothing but Jensen's inequality for a convex function $-S$. Although (22.1) never happens to equilibrium states (if internal constraints are respected), in contrast to it, (22.2) may be understood as the stability condition.

22.3 Stability condition for general systems due to convexity

To study the effects of thermodynamic variations applied to a non-isolated system, we use the usual trick to regard the system S to be a part of a very large isolated system (Fig. 22.1), whose part other than the system itself is called the *reservoir*.[305] Then, for the total big isolated system, (22.1) tells us

$$\Delta S + \Delta S_{\rm res} \le 0, \tag{22.3}$$

where Δ denotes a thermodynamic variation that respects the system/reservoir distinction. As noted at the end of **22.2** this is due to the convexity of the (negative) total entropy, and *not* due to the stability of the equilibrium system.

In the reservoir the values of the conjugate variables of the thermodynamic coordinates are kept constant and identical to those of the system before thermodynamic variations. The extensive quantities may be exchanged freely between the system and its surrounding bath. Let us assume that the system obtains extensive quantities ΔE, ΔV, ΔX, ΔN, etc., by the variation.[306]

For the reservoir portion, all the intensive quantities are constant, and we obtain

$$\Delta S_{\rm res} = -\frac{1}{T_e}\Delta E - \frac{P_e}{T_e}\Delta V + \sum \frac{x_e}{T_e}\Delta X + \sum \frac{\mu_e}{T_e}\Delta N, \tag{22.4}$$

---

[305] If you argue that assuming such a big system called a reservoir is theoretically dubious, you must prepare increasing sequence of reservoirs to construct your theory. Alternatively, we may utilize special materials that can maintain conjugate variables of the operational coordinates (see, for example, **8.8**).

[306] Here, we have assumed that all the thermodynamic coordinates may be freely exchanged, but we can certainly consider more restricted cases such as only internal energy and volume may be exchanged. To obtain the formulas for such cases, simply suppress coordinates not exchanged between the system and the bath from the following formulas, in particular from (22.5).

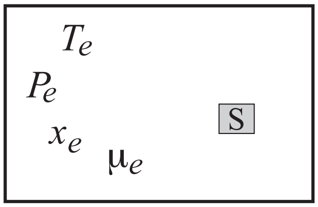

Figure 22.1: The system S is a small part of a very large isolated system. The intensive quantities T_e, P_e, etc., are kept constant, because the total isolated system is very large. Their conjugate extensive quantities (S, V, etc.) may be assumed to be exchanged freely between the system and its surrounding portion of the total system call the reservoir.

where X and N denote various work coordinates (other than V) and materials coordinates, respectively. We assume chemostats are separately prepared for each chemical.[307]

For the system S its intensive quantities may be altered by thermodynamic variations, so we cannot obtain ΔS simply as (22.4), i.e., the change of the extensive quantities alone. The entropy of the total system is $\Delta S + \Delta S_{\rm res}$, so the inequality (22.3) implies

$$\Delta S - \frac{1}{T_e}\Delta E - \frac{P_e}{T_e}\Delta V + \sum \frac{x_e}{T_e}\Delta X + \sum \frac{\mu_e}{T_e}\Delta N \le 0. \tag{22.5}$$

This is the result of convexity.

Remark In (22.5) ΔN is the exchange between the system and the surrounding reservoir, and has nothing to do with the existence of chemical reactions in the system or not. If chemical reactions occur in the system, we only need $\Delta\tilde{\boldsymbol{N}} \neq \Delta\boldsymbol{N}$ if we describe the change in terms of chemical compositions (recall **4.9**). However, since ΔE, ΔX, etc., are not generally zero, there is no guarantee that $\boldsymbol{\mu}_e \cdot \Delta\tilde{\boldsymbol{N}} = \boldsymbol{\mu}_e \cdot \Delta\boldsymbol{N}$ holds.

22.4 The universal local stability criterion for an equilibrium state

If the thermodynamic variation Δ is not large for the reservoir, it may be written in terms of small thermodynamic variation δ as

$$\Delta S_{\rm res} = -\frac{1}{T_e}\delta E - \frac{P_e}{T_e}\delta V + \frac{x_e}{T_e}\delta X + \sum \frac{\mu_e}{T_e}\delta N. \tag{22.6}$$

The variation of the system entropy ΔS may be (Taylor) expanded in terms of the

---

[307] As we have seen in **4.8** we may not ignore 'intrinsically accompanying compounds', so even the so-called pure substance may not exclude chemical reactions, but usually, we ignore them.

small thermodynamic variation δ as:[308]

$$\Delta S = \delta S + \delta^2 S + \cdots . \tag{22.7}$$

The first order term may be computed in terms of the derivatives in the original equilibrium state, so we may write

$$\delta S = \frac{1}{T_e}\delta E + \frac{P_e}{T_e}\delta V - \frac{x_e}{T_e}\delta X - \sum \frac{\mu_e}{T_e}\delta N. \tag{22.8}$$

This formula and (22.6) imply that for small thermodynamic perturbations applied to the equilibrium state (22.3) can always be expressed as

$$\delta^2 S \le 0 \tag{22.9}$$

irrespective of the environment of the system. Note that this may be obtained immediately from the concavity of entropy for small thermodynamic variations.[309] It is universal, but only for small thermodynamic perturbations.

22.5 The universal local stability condition in terms of internal energy variation

(22.5) may be rewritten as

$$\Delta E - T_e \Delta S + P_e \Delta V - x_e \Delta X - \mu_e \Delta N > 0. \tag{22.10}$$

If we Taylor expand ΔE just as we did for ΔS in **22.4**, with the same logic we can obtain a universal local stability criterion

$$\delta^2 E \ge 0 \tag{22.11}$$

which is equivalent to (22.9). Notice that this inequality can also be obtained immediately from the convexity of E (→**13.10**).[310]

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[308] Notice that, since the reservoir is huge compared with the system itself, the first order approximation for the reservoir is much more accurate than that for the system; for example, the constancy of the first derivatives is much less accurate for the system than for the reservoir, requiring higher order terms.

[309] If there are non-additive work coordinates, such a universal result cannot be asserted.

[310] However, just as the case of the entropy inequality (22.9), if there are non-additive work coordinates, the stability against their variation cannot be obtained this way.

22.6 A positive definite quadratic form given by the Hessian of *E*

If we write all the standard variables of E: S, X, and N as $Y = \{Y_i\}$, (22.11) can be written as a positive definite quadratic form of δY_i:

$$\delta^2 E = \sum_{i,j} \frac{\partial^2 E}{\partial Y_i \partial Y_j} \delta Y_i \delta Y_j \geq 0. \tag{22.12}$$

For example,

$$(\delta S, \delta V, \delta N) \begin{pmatrix} \left(\frac{\partial T}{\partial S}\right)_{V,N} & \left(\frac{\partial T}{\partial V}\right)_{S,N} & \left(\frac{\partial T}{\partial N}\right)_{S,V} \\ -\left(\frac{\partial P}{\partial S}\right)_{V,N} & -\left(\frac{\partial P}{\partial V}\right)_{S,N} & -\left(\frac{\partial P}{\partial N}\right)_{S,V} \\ \left(\frac{\partial \mu}{\partial S}\right)_{V,N} & \left(\frac{\partial \mu}{\partial V}\right)_{S,N} & \left(\frac{\partial \mu}{\partial N}\right)_{S,V} \end{pmatrix} \begin{pmatrix} \delta S \\ \delta V \\ \delta N \end{pmatrix} \geq 0. \tag{22.13}$$

22.7 A positive definite condition for the quadratic form

Let $A = \text{matr}(A_{ij})$ be a $n \times n$ symmetric square matrix. A necessary and sufficient condition for the quadratic form

$$\sum A_{ij} x_i x_j \tag{22.14}$$

to be positive definite is that all of its principal minors are positive:

$$\det(A_{kl}) \geq 0, \tag{22.15}$$

where $\text{matr}(A_{kl})$ is with k and l chosen in the same order from a subset $U \subset \{1, 2, \cdots, n\}$.

22.8 Le Chatelier's principle

Since the Hessian of E is nonnegative definite, as seen from **22.7**, all the diagonal elements are nonnegative:

$$\left(\frac{\partial^2 E}{\partial Y_i^2}\right)_{Y_i^c} \geq 0. \tag{22.16}$$

That is, writing the conjugate intensive quantity of Y_i as y_i

$$\left(\frac{\partial y_i}{\partial Y_i}\right)_{Y_i^c} \geq 0. \tag{22.17}$$

This is called Le Chatelier's principle.

Since the sign of the inverse determinant is also the same, we get

$$\left(\frac{\partial Y_i}{\partial y_i}\right)_{Y_i^c} \geq 0., \tag{22.18}$$

but notice that this is not $(\partial Y_i/\partial y_i)_{y_i^c} \geq 0$. For example, $C_V > 0$ may be obtained from (22.18), but this does not immediately imply $C_P > 0$.[311]

22.9 More general Le Chatelier's principle

The heat capacity should be positive irrespective of the conditions. This implies that

$$\left(\frac{\partial S}{\partial T}\right)_Z \geq 0, \tag{22.19}$$

where Z is the set of variables chosen one variable from each conjugate pair other than (S, T). We can demonstrate this inequality, starting from the case for all Z being extensive variables inductively[312] (→**22.10**, **22.11**). However, the cleverest way is to go back to $\delta^2 E > 0$. This may be expressed (→**9.11**(iii)) as

$$\delta^2 E = \delta T \delta S - \delta P \delta V + \delta x \delta X + \sum \delta\mu \delta N > 0, \tag{22.20}$$

so changing independent variables corresponds to choosing δx or δX from each pair $\delta x \delta X$. Then, (22.19) should be obvious.

Le Chatelier's principle indicates that the world we usually live, which is rather close to equilibrium, is stable. Imagine what could happen, if the inequality in Le Chatelier's principle were flipped.

22.10 Stability condition under all the conjugate intensity variables are fixed

To begin with we demonstrate the following inequality. Here, the suffixes y_i^c for the partial derivative implies that all the conjugate intensive variables other than y_i are fixed:

$$\left(\frac{\partial y_i}{\partial Y_i}\right)_{y_i^c} \geq 0, \ \left(\frac{\partial Y_i}{\partial y_i}\right)_{y_i^c} \geq 0 \tag{22.21}$$

---

[311] (22.18) tells us that $(\partial S/\partial T)_V = C_V/T > 0$, but we have not yet discussed the sign of $(\partial S/\partial T)_P$.

[312] However, this approach is so cumbersome that, except for calculation practice, you should not follow it.

Indeed (note that in the following Jacobians (y_i, y_i^c) does not mean two variables but general n variable formulas)

$$\left(\frac{\partial y_i}{\partial Y_i}\right)_{y_i^c} = \frac{\partial(y_i, y_i^c)}{\partial(Y_i, y_i^c)} = \frac{\partial(y_i, y_i^c)}{\partial(Y_i, Y_i^c)}\frac{\partial(Y_i, Y_i^c)}{\partial(Y_i, y_i^c)}, \tag{22.22}$$

but the left factor in the rightmost formula is the Hessian matrix of E itself, so it is positive. The right factor must compute partial derivatives regarding $\{Y_i, y_i^c\}$ as independent variables, so $\partial Y_i/\partial y_k = 0$. Consequently, the first column becomes $(1, 0, \cdots)^t$. Thus, this factor is equal to the determinant of $(n-1)\times(n-1)$ which is the principle minor of the original Hessian matrix except for the first raw and column. Thus, it is positive (→**22.6**)

22.11 Exchange of upper- and down-stairs of general $n \times n$ Hessian

More generally, $(\partial y/\partial Y)_{\rm cond}$ is nonnegative under any condition ('cond' $= z = \{z_1, \cdots, z_n\}$ (z_i^c implies to remove z_i); Here, $z_j = y_j$ or Y_j) and Z is the conjugate of z. We have

$$\left(\frac{\partial y_i}{\partial Y_i}\right)_{z} = \frac{\partial(y_i, z_i^c)}{\partial(Y_i, z_i^c)} = \frac{\partial(y_i, z_i^c)}{\partial(Y_i, Z_i^c)}\frac{\partial(Y_i, Z_i^c)}{\partial(Y_i, z_i^c)}. \tag{22.23}$$

The first factor in the right most term is the Hessian of E itself, so it is nonnegative. The second factor requires to calculate the partial derivatives regarding $\{Y_i, z_i^c\}$ as independent variables. Since $\partial Y_i/\partial z_k = 0$, we must demonstrate

$$\frac{\partial(z)}{\partial(Z)} \geq 0 \tag{22.24}$$

for the $(n-1)\times(n-1)$ principal minor constructed by removing the first raw and colum from $\partial(Y_i, Z_i^c)/\partial(Y_i, z_i^c)$. To show this we can step by step exchange the variable in the numerator with the corresponding conjugate in the denominator and show this procedure does not change the sign of the Jakobian.

The first step is as follows ($z = y$ or Y is the starting point). We have

$$\frac{\partial(x, z)}{\partial(X, Z)} = \frac{\partial(x, z)}{\partial(X, z)}\frac{\partial(X, z)}{\partial(x, Z)}\frac{\partial(x, Z)}{\partial(X, Z)} = \left(\frac{\partial x}{\partial X}\right)_z\left(\frac{\partial x}{\partial X}\right)_Z\frac{\partial(X, z)}{\partial(x, Z)}, \tag{22.25}$$

As we have seen in (22.17) and (22.21) the two partial derivatives in the right-most formula is nonnegative, we see the $n \times n$ determinant obtained by exchanging x and X is nonnegative. The resultant $n \times n$ matrix is nonnegative definite, its diagonal elements are nonnegative. Thus, we may repeat the same argument as above for the case with one pair exchanged between numerator and denominator. That is, inequalities similar to (22.17) and (22.21) holds for one pair of conjugate variables exchanged between numerator and denominator. We can repeat this argument, so we may exchange as many conjugate variables between numerator and denominator.

22.12 Le Chatelier-Braun's principle

We know $C_P > C_V$ for the ideal gas due to Mayer's relation, but actually this is an example of the universal inequality:

$$\left(\frac{\partial X}{\partial x}\right)_y \geq \left(\frac{\partial X}{\partial x}\right)_Y . \tag{22.26}$$

This can be demonstrated as follows.

$$\begin{aligned}
\left(\frac{\partial X}{\partial x}\right)_y &= \frac{\partial(X,y)}{\partial(x,y)} = \frac{\partial(X,y)}{\partial(x,Y)}\frac{\partial(x,Y)}{\partial(x,y)} && (22.27)\\
&= \left[\left(\frac{\partial X}{\partial x}\right)_Y \left(\frac{\partial y}{\partial Y}\right)_x - \left(\frac{\partial X}{\partial Y}\right)_x \left(\frac{\partial y}{\partial x}\right)_Y\right] \left(\frac{\partial Y}{\partial y}\right)_x && (22.28)\\
&= \left(\frac{\partial X}{\partial x}\right)_Y - \left(\frac{\partial X}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_Y . && (22.29)
\end{aligned}$$

(22.29) implies

$$\left(\frac{\partial X}{\partial y}\right)_x = \frac{\partial(X,x)}{\partial(y,x)} = \frac{\partial(X,x)}{\partial(y,Y)}\frac{\partial(y,Y)}{\partial(x,Y)}\frac{\partial(x,Y)}{\partial(y,x)} = -\left(\frac{\partial y}{\partial x}\right)_Y \left(\frac{\partial Y}{\partial y}\right)_x , \tag{22.30}$$

so

$$\left(\frac{\partial X}{\partial x}\right)_y = \left(\frac{\partial X}{\partial x}\right)_Y + \left(\frac{\partial Y}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_Y^2 . \tag{22.31}$$

Since the second term on the right-hand side is nonnegative,

$$\left(\frac{\partial X}{\partial x}\right)_y \geq \left(\frac{\partial X}{\partial x}\right)_Y . \tag{22.32}$$

For example, for $X = S$

$$C_P \geq C_V . \tag{22.33}$$

Or for $X = V$, $x = -P$ so we have an inequality about the compressibility:

$$\kappa_T \geq \kappa_S . \tag{22.34}$$

What if Le Chatelier-Braun's principle does not hold? As can be seen from (22.31) then the Le Chatelier's principle for the conjugate pair appearing in the conditions (that is, for y and Y) is violated. That is, Le Chatelier-Braun's principle does not give any constraints substantially different from Le Chatelier's principle.

22.13 Constraints on the changes due to phase transitions

If a phase transition occurs, E need not be twice differentiable. Consequently, we cannot use (22.17). Note that Le Chatelier's principle is a direct consequence of the convexity of E. Even without sufficient differentiability, convexity still imposes strong constraints on the changes of quantities around the phase transition. For example, if we compare the low temperature phase and the high temperature phase, the latter is expected to be with larger entropy. Such a relation can be concluded from the gradient inequality (D.20); Let (x, X) be the conjugate pair. Then, if other variables are kept constant, we have

$$\Delta x \Delta X \geq 0. \tag{22.35}$$

Therefore, for example, we get

$$\Delta T \Delta S \geq 0, \tag{22.36}$$

which supports the above expectation. We can also obtain the following natural inequality:

$$\Delta P \Delta V \leq 0. \tag{22.37}$$

23 Phase transitions

23.1 Phases and phase diagrams: outline

A substance may exhibit qualitatively different properties under various conditions (say, under different (T, P)). Roughly speaking, if we observe such a situation, we say the substance is in different phases (→**23.2** more precisely). Liquid water, ice and vapor are different phases of water. "Qualitatively different properties" mean, for example, "pushing one end of the system moves the other end" (the existence of a long-range order), or "compressing does not visibly shrink the system" (coherence) (see the table below).

	long-range order	coherence
solid phase	YES	YES
liquid phase	NO	YES
gas phase	NO	NO

To understand a substance begins with knowing its various phases and their characteristic features. Thus, to begin with, we wish to make a sort of a map of the thermodynamic space (or at least the space spanned by some thermodynamic variables such as T and P) indicating the phase of the substance at each point on the map. This map is called the *phase diagram* (see, for example, Fig. 23.1).

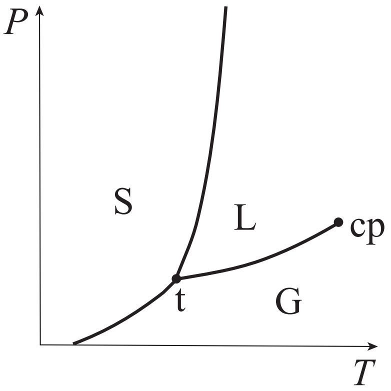

Figure 23.1: A representative phase diagram of an ordinary fluid

Fig. 23.1 A representative phase diagram of an ordinary fluid. S: solid phase; L: liquid phase; G: gas phase; t: triple point; cp: critical point. The curves indicate the phase boundaries, where phase transitions occur. The boundary between L and G ends at cp, so even if 'fluid phase' (= non-solid phase) may be defined globally, liquid phase or gas phase cannot be globally defined.

23.2 What is a phase?

Defining "phase" precisely is not a trivial task. Near a phase boundary coexisting phases may be clearly distinguished, but the region where a particular phase occupies may not be clearly defined as already pointed out for the gas and liquid phases of an ordinary fluid in Fig. 23.1. Furthermore, even if a clear boundary exists in the phase diagram we see, the diagram might be a low-dimensional section of a more complete high-dimensional phase diagram, in which some of the phase boundaries might disappear along the axis perpendicular to the diagram shown to us. Therefore, when we use the word 'phase' precisely, we should do so with respect to the phase diagram shown to us and locally, meaning that in a local region of the given phase diagram. 'The two phases are distinct, only if they can change into each other across the phase boundary where phase transitions occur."

23.3 What is a phase transition?

For a given system, its equilibrium state is uniquely mapped to a point in its thermodynamic space (→**5.2**). Even if the system has the coexistence of several phases, its state is still uniquely mapped to a point in its thermodynamic space.

To illustrate this, let us draw the phase diagram of an ordinary fluid in its thermodynamic space (Fig. 23.2).

Fig. 23.2 A schematic phase diagram of an ordinary fluid in its thermodynamic space

The white dots are critical point (in both diagrams). The black small square (left) and the dark gray triangle (right) indicate the triple point. The pale gray regions represent the two-phase coexistence regions. The primary purpose of this figure is to illustrate that the coexistence lines and triple point in the usual phase diagram (left inset) are unfolded into regions corresponding to various ratios of coexisting phases; we can actually know the coexistence ratio of various phases from the diagram.

For example, take the solid-gas coexisting region S + G. The black dot 's' on the solid-phase boundary indicates a pure solid phase with a definite (E, V) coordinates, and the black dot 'g' on the gas-phase boundary indicates a particular gas phase with a definite (E, V) (The figure also contains another pair s' and g' to exhibit another solid-gas coexisting relationship).

The white square on the line connecting s and g can express a particular ratio of these two coexisting phases. If the white square is located at the point with the line segment length ratio $\alpha : (1 - \alpha)$, then the coexistence state consists of sold phase 's' and gas phase 'g' in the ratio

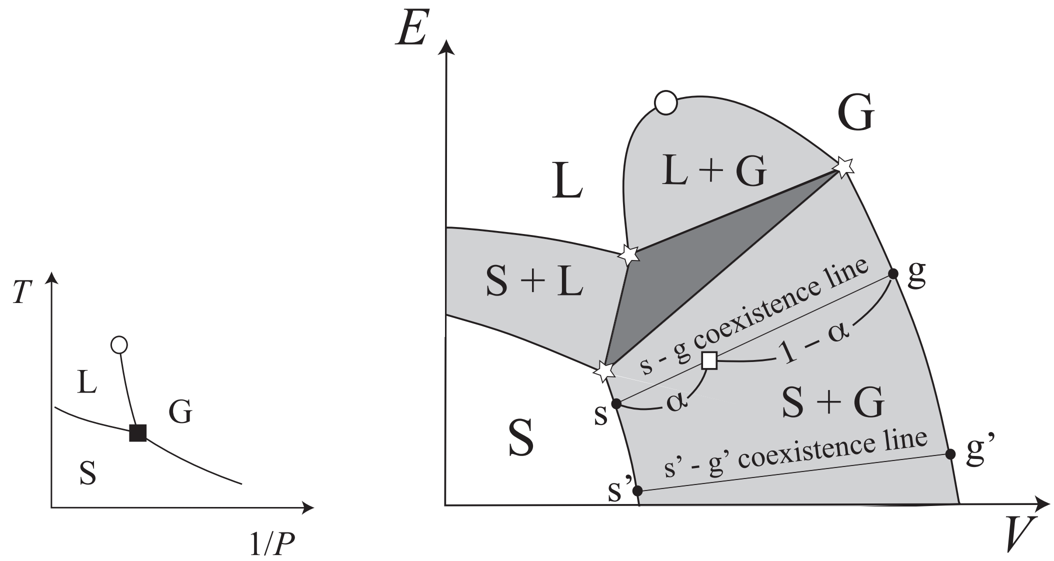

Figure 23.2: Phase diagram in the thermodynamic space. The white dot is a critical point, the black dot and the dark triangular region indicate a triple point (= three-phase coexisting states). The gray regions are two-phase coexisting states. It is a conceptual illustration, but the key point is that coexistence lines and a triple point in the usual phase diagram (left inset) are unfolded into regions corresponding to various ratio of coexisting phases.

$(1-\alpha):\alpha$; This is known as the *lever rule*. Similar lines can be drawn in the solid-liquid coexistence state. Thus, the coexistence region is a ruled surface in the thermodynamic space.

The position of any point in the dark gray representing three-phase coexistence phase expressed in the barycentric coordinates of three white stars, uniquely indicating the states of the coexisting three phases.

In this 2-dimensional phase diagram thermodynamic variables are, especially internal energy is, twice differentiable with respect to S and V in the areas corresponding to individual phases. This smoothness is reduced at the phase boundaries; while E never loses continuous differentiability, its derivatives are generally not differentiable. It is important to note that a change in smoothness of E is necessary for qualitative changes to occur. However, if multiple phases coexist (as in the light or dark gray regions in Fig. 23.2), then E is again smooth.

Therefore, a mathematically clearcut characterization of a phase transition may be (1) Phase coexistence of (2) some loss of smoothness of E as a function of S and operational coordinates $\boldsymbol{Y}$.[313] Accordingly, the (local) definition of phase in **23.2** is

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[313] One could say that a phase transition occurs, if a certain complete thermodynamic function (→**18.12**) becomes less differentiable than in the bulk phases. Statistical mechanically one could

mathematically clear.

23.4 First order and second order phase transitions

Phase transitions are often classified into two categories: the first order phase transitions and the rest, called continuous or second order phase transitions. In first-order phase transitions at least one thermodynamic density (→**5.5**) changes discontinuously as a function of the conjugate thermodynamic field (→**5.5**), but for second order phase transitions there is no jump in thermodynamic densities. Gas-liquid phase transitions are usually first order, but under critical pressure, they become second-order.

In many interesting examples, phase transitions occur between ordered and not so ordered phases; we could say transitions occur between low entropy phases and high energy phases. For example folding of proteins usually occur between high energy random-coil states and low entropy folded states.

Intuitively, a first order phase transition occurs, if the stability of an ordered phase is lost catastrophically. In other words, if slight reduction of order induces its further reduction, a first-order phase transition occurs. Consequently, it is impossible to observe an equilibrium state with reduced order.

In contrast, for a second order phase transition, the above mentioned positive feedback loop of order reduction does not exist. Therefore, it is possible to observe equilibrium states with reduced order. An equilibrium state with reduced order may be intuitively analogized with an oscillator with a reduced spring constant, whose fluctuations become enhanced. Even if fluctuations become large, the ordered state endures them. Since the existence of a sort of order and its disappearance are characteristic features of phase transitions, second order phase transitions become theoretically very interesting.

23.5 Phase coexistence: the case of two phases

Let us assume that an isolated system (without chemical reactions) is described by the thermodynamic coordinates (E, X), and phase I and phase II coexist under the condition to exchange E and X. We follow the argument in **19.8**. We must maximize the system entropy $S = S_{\mathrm{I}} + S_{\mathrm{II}}$ under the exchange of E and V (→**12.4**). Gibbs'

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say that phase transition occurs if a certain complete thermodynamic function loses holomorphy. However, experimentally, 'holomorphy' seems impossible to demonstrate, let alone analyticity.

relation reads

$$dS = \frac{1}{T}dE - \frac{x}{T}dX - \frac{\mu}{T}dN, \tag{23.1}$$

so, if δ denotes virtual variations (actually changes realized by fluctuations), the equilibrium condition becomes

$$\delta S = \frac{1}{T_{\rm I}}\delta E_{\rm I} - \frac{x_{\rm I}}{T_{\rm I}}\delta X_{\rm I} - \frac{\mu_{\rm I}}{T_{\rm I}}\delta N_{\rm I} + \frac{1}{T_{\rm II}}\delta E_{\rm II} - \frac{x_{\rm II}}{T_{\rm II}}\delta X_{\rm II} - \frac{\mu_{\rm II}}{T_{\rm II}}\delta N_{\rm II} = 0. \tag{23.2}$$

Since $\delta E_{\rm I} + \delta E_{\rm II} = 0$, $\delta X_{\rm I} + \delta X_{\rm II} = 0$, $\delta N_{\rm I} + \delta N_{\rm II} = 0$, (23.2) becomes

$$\delta S = \left(\frac{1}{T_{\rm I}} - \frac{1}{T_{\rm II}}\right)\delta E_{\rm I} - \left(\frac{x_{\rm I}}{T_{\rm I}} - \frac{x_{\rm II}}{T_{\rm II}}\right)\delta X_{\rm I} - \left(\frac{\mu_{\rm I}}{T_{\rm I}} - \frac{\mu_{\rm II}}{T_{\rm II}}\right)\delta N_{\rm I}, \tag{23.3}$$

so, generally, the following equalities are required:

$$T_{\rm I} = T_{\rm II},\ x_{\rm I} = x_{\rm II},\ \mu_{\rm I} = \mu_{\rm II}. \tag{23.4}$$

The most common cases are with $X = V$ and $x = -P$, so the condition for the chemical potentials is

$$\mu_{\rm I}(T,P) = \mu_{\rm II}(T,P), \tag{23.5}$$

which determines the phase coexisting curves in the TP phase diagram.[314]

This relation may be obtained from the principle of Gibbs energy minimization under constant TP condition. From (23.5) we derived Clapeyron-Clausius's equation (→**19.9**).

The Gibbs energy of the system is given by

$$G = N_{\rm I}\mu_{\rm I} + N_{\rm II}\mu_{\rm II}. \tag{23.6}$$

Therefore, the state can change without changing G (only $N_{\rm I}$ and $N_{\rm II}$ vary; note $N_{\rm I} + N_{\rm II} =$ constant). Consequently, the TP phase coexisting line becomes an area in the thermodynamic space as we have seen in Fig. 23.2.

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[314] Precisely speaking, E, V and N, and not T and P, are the thermodynamic variables in the current situation of an isolated system. Thus, T, P and μ are functions of E, V and N. Therefore, to obtain (23.5), we must write E_n, V_n and N_n ($n =$ I or II) in terms of T and P, and then convert $\mu(E,V,N)$ to a function of T and P. As stated just below, the result can be obtained directly with the aid of the variational principle for G.

23.6 The direction of changes due to phase transitions

We have already seen in **22.13** that being in equilibrium implies for any conjugate pair (x, X) there is a constraint:

$$\Delta x \Delta X \geq 0. \tag{23.7}$$

Since this is not usually discussed in elementary textbooks, let us repeat it with examples.

If the changes are not zero, then $\Delta P \Delta V < 0$ or

$$(P_{\mathrm{II}} - P_{\mathrm{I}})(V_{\mathrm{II}} - V_{\mathrm{I}}) < 0. \tag{23.8}$$

This requires that the low pressure phase must have larger volume/material quantity (say, molar volume). If we take freezing of water around 1 atm as an example, ice has a larger molar volume than liquid water. This is consistent with the fact that we can melt ice at a constant temperature by applying pressure.

$\Delta T \Delta S \geq 0$ implies that if there is a system that can solidify upon increasing its temperature, the entropy of the solid phase must be larger than that of the fluid phase. This actually happens in ^{3}He (Fig. 23.3; the transition along the red arrow).

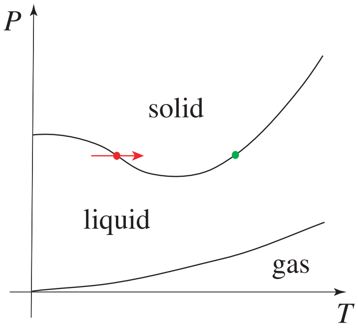

Figure 23.3: The Pomeranchuk effect

Fig. 23.3 The Pomeranchuk effect: if we raise temperature at the red spot, the liquid phase solidifies. Therefore, the solid phase must have a larger entropy than the liquid phase. In this case, the reason why the solid phase has a larger entropy is that the nuclear spins are not ordered in the solid phase. The spins exhibits a antiferromagnetic order below 10^{-3} K. At the green spot, the solid phase has a smaller entropy than the liquid phase just as the ordinary systems.

23.7 Thermodynamic phases when symmetry breaks spontaneously

Suppose a magnet becomes a ferromagnet. Then, its non-zero magnetization can point many directions. Ideally, all the directions have the same energy, so it is just as the case of the shape unrelated to the system energy. That is, the direction of the magnetization vector $\boldsymbol{M}$ is an example of macroobservables that need not be distinguished thermodynamically.

Of course, in practice, the magnetization directions are important, but that is not relevant energetically.[315]

23.8 Phase equilibrium of a pure substance

Suppose ϕ phases (I, II, $\cdots, \phi$) coexist. Let μ_{x} be the chemical potential of phase x. Then, the following $\phi - 1$ equations must be satisfied:

$$\mu_{\mathrm{I}}(T, P) = \mu_{\mathrm{II}}(T, P) = \cdots = \mu_{\phi}(T, P). \tag{23.9}$$

Assume that there is no special functional relations among the chemical potentials of the phases. Then, (23.9) gives $\phi - 1$ independent conditions. For these equations to have solutions T and P there should be at most two independent equalities. Thus, for a pure substance, at most three phases ($\phi = 3$) can coexist.

If three phases coexist, then the T and P are unique (locally in the phase diagram, →**23.10** (2)). This point is called the *triple point*. Until 2019 the Kelvin temperature was defined by fixing the triple point of pure water to be $T = 273.16$ K.[316]

23.9 Gibbs' phase rule

Let us consider a system consisting of c chemical species that are regarded independent (→**4.5**; it is assumed that there is no reaction).

If ϕ phases coexist, the phase equilibrium conditions are:

(1) T and P are common to all the phases

(2) For each of the c independent chemicals the chemical potential is identical for all the phases. Thus, as we have seen in (23.9), each chemical must satisfy $\phi - 1$

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[315] If there is an external magnetic field $\boldsymbol{B}$, then $\boldsymbol{M}$ is energetically relevant. However, in this case, in equilibrium, there is only one particular $\boldsymbol{M}$ fixed. In any case, we need not consider the coexistence of continuously many phases.

[316] The unit K is now (since 2019 or at the 26th General Conference on Weights and Measures in late 2018) defined with a value of the Boltzmann constant to be fixed as $k_B = 1.380649 \times 10^{-23}$ J·K^{-1}. The unit J·K^{-1} = kg·m^2·s^{-2}·K^{-1}, where the kilogram, meter and second are defined in terms of the Planck constant, the speed of light, and the duration of the caesium-133 ground-state hyperfine transition, respectively.

equations ($j = 1, \cdots, c$):

$$\mu^j_{\rm I}(T, P, x^1_{\rm I}, x^2_{\rm I}, \cdots x^{c-1}_{\rm I}) = \mu^j_{\rm II}(T, P, x^1_{\rm II}, x^2_{\rm II}, \cdots x^{c-1}_{\rm II}) = \cdots = \mu^j_{\phi}(T, P, x^1_{\phi}, x^2_{\phi}, \cdots x^{c-1}_{\phi}). \tag{23.10}$$

Consequently, the number of equalities that must be satisfied is $(\phi - 1) \times c$.

To determine the composition of each phase, its $c-1$ mole fractions $(x^1, x^2, \cdots, x^{c-1})$ must be known.[317] The compositions are different from phase to phase, so we must determine $\phi \times (c - 1)$ mole fractions $x^1_{\rm x}, x^2_{\rm x}, \cdots x^{c-1}_{\rm x}$ ($\rm x = 1, \cdots, \phi$, if we distinguish phases with suffixes). Therefore, to determine the state of the system, we must determine $2 + \phi(c - 1)$ variables, T, P and $x^j_{\rm x}$ ($j = 1, \cdots, c - 1$, $\rm x = 1, \cdots, \phi$). Therefore, in the generic case the number of variables remaining undetermined is $f = 2 + \phi(c - 1) - c(\phi - 1) = c + 2 - \phi$. That is, even with the coexisting condition constraints, still (T, P) can move in the region of dimension f in the phase space:

$$f = c + 2 - \phi. \tag{23.11}$$

This f is called the *thermodynamic freedom*, and the formula is called *Gibbs' phase rule*.

For a pure substance $c = 1$ gives $f = 3 - \phi$. Thus, if two phases coexist, $f = 1$, that is, the coexisting states make a 1 dimensional shape on the T, P diagram (i.e., coexisting curve). If three phase coexist, then $f = 0$, meaning the coexisting phase makes a zero-dimensional shape (i.e., triple point).

23.10 Remarks on phase coexistence

(1) As can be seen from the derivation of the phase rule, the coexistence is discussed under the condition of genericity; there are no 'accidental' relations among functions. Therefore, mixtures or even pure chemicals can violate the phase rule, i.e., substances for which f is larger than that dictated by the phase rule (23.11) can be realized.[318]
(2) Does the phase rule hold globally for the phase diagram? No. For example, a problem such as the number of crossing points between two curves in the plane cannot be answered by a crude argument utilized in the derivation of the phase rule.

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[317] The mole fraction x_i of chemical i is defined by $x_i = \tilde{N}_i / \sum_{j=1}^c \tilde{N}_j$. In this case, no chemical reaction is assumed to occur, so we can also define x_i in terms of materials coordinates as $x_i = N_i / \sum_{j=1}^c N_j$.

[318] Indeed, it is possible to make a pure substance with quadruple point. For example, K. Akahane, J. Russo and H. Tanaka, A possible four-phase coexistence in a single-component system, Nature Commun. **7** 12599 (2017).

Therefore, we cannot answer how many triple points a given substance has. Two triple points could exist very close with each other; we would not be surprised, if they merged.

(3) Then, when the phase rule predict the coexistence, can the coexistence actually occur? For the phases that thermodynamics can distinguish, the coexistence would happen. However, if the phases are due to a spontaneous symmetry breaking, can they coexist? This depends on the stability of the interface, for example, and is not a concern of thermodynamics (→**23.7**).

(4) Then, are actually coexisting phases equilibrium phases and is the coexistence true equilibrium? This is not a simple question. Liquid-liquid phase separations in a cell or the resultant intracellular membraneless organelles need not be in equilibrium. Or, the folded states of proteins should be considered as distinct phases from the random states, and the transitions between them are first-order like.[319] However, nonequilibrium cases should not be rare; biologically meaningful states can be nonequilibrium states with the true equilibrium state rarely attained, or even the true equilibrium state could be harmful for organisms. Think of prions.

23.11 Legendre-Fenchel transformation with phase transitions

18.11 tells us that the Helmholtz energy can be obtained by a Legendre-Fenchel transformation of the internal energy as

$$-A(T) = \max_S |_{\boldsymbol{Y}} [TS - E(S, \boldsymbol{Y})] = \sup_S |_{\boldsymbol{Y}} [TS - E(S, \boldsymbol{Y})]. \tag{23.12}$$

That is, we have seen

$$-A = E^*. \tag{23.13}$$

This allows the inverse transformation; the convexity of E allows

$$(-A)^* = E^{**} = E. \tag{23.14}$$

Thus, the Helmholtz energy A is a complete thermodynamic function (→**18.12**).

However, is temperature T not a proper thermodynamic coordinate (→**3.8**)? Still do we not lose any information that the internal energy has when it is transformed to the Helmholtz energy? This is a reasonable question. The answer is: E as a function is completely reconstructed from A, but the original value of S cannot be recovered.

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[319] This is a fact pointed out first by N. Gō.

That is, there is lost information due to using non-fundamental thermodynamic variables.

Let us assume that the original state has entropy S with temperature T. As we have seen in the thermodynamic phase diagram Fig. 23.2 with a given T various S can associate. By the transformation $E \to -A$ all the state with the same temperature are mapped to a single point, so naturally, the actual original entropy value is lost. Still, the range of the values of entropy associated with a given T is perfectly recovered (see Fig. 23.4).[320]

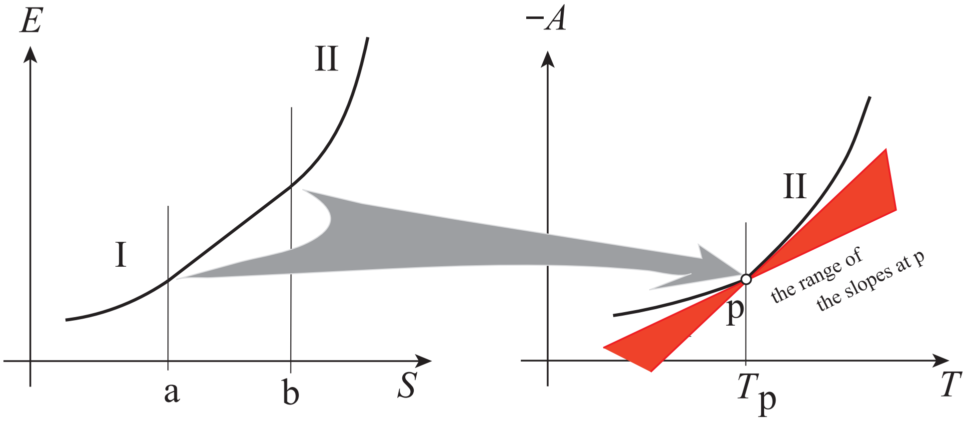

Figure 23.4: Between a and b entropy changes but the temperature is constant. Then, the graph of E is with a constant slope between a and b. This portion is mapped by the Legendre-Fenchel transformation to a point p with the temperature given by the slope (and A becomes non-differentiable). However, the range of the slope of the lines tangent to $-A$ at p (i.e., the red fan) is not lost from the graph of A and can be restored. Needless to say, we cannot tell from which point the arrow started. This is the reason why T is not a fundamental thermodynamic variable.

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[320] Convex analytically, we say it is determined as the *subdifferential* (→**D.3**) of A with respect to T.

24 The third law of thermodynamics

24.1 Determination of the Gibbs energy: motivation for the third law

From the late 19th to the early 20th century, an important question of chemical physics/chemistry was to determine the free-energy change ΔG of a chemical reaction[321] in terms of the reaction heat ΔH. The 'Thomsen-Berthelot principle'[322] was interpreted as $\Delta G = \Delta H$ in the thermal theory of affinity.[323]

According to this theory no endothermic process can proceed spontaneously as pointed out by Helmholtz (1882). Deriving the Gibbs-Helmholtz equation (19.7), he showed that generally $\Delta G \neq \Delta H$:

$$\Delta H = \Delta G - T\left(\frac{\partial \Delta G}{\partial T}\right)_P . \tag{24.1}$$

Integrating the Gibbs-Helmholtz equation (19.7) in the form: $\Delta H/T^2 = -(\partial(\Delta G/T)/\partial T)_P$, we obtain

$$\Delta G = -T\int_{T_0}^{T} \frac{\Delta H}{T^2} dT + \frac{\Delta G(T_0)}{T_0} T. \tag{24.2}$$

That there was no way to determine $\Delta G(T_0)/T_0$ from the reaction heat ΔH was the central difficulty of chemical thermodynamics according to Nernst.[324]

24.2 Nernst's proposal

Nernst asserted that ΔG and ΔH are not generally equal, but at sufficiently low temperatures they are very close. Therefore, close to $T = 0$, the equality must be

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[321] Or, the affinity $-\Delta G$ of a chemical reaction.

[322] Julius Thomsen (1826-1909), `https://en.wikipedia.org/wiki/Hans_Peter_Jrgen_Julius_Thomsen` ; Marcellin Berthelot (1827-1907) `https://en.wikipedia.org/wiki/Marcellin_Berthelot`. This principle claims: all chemical changes are accompanied by the production of heat and processes which actually occur will be ones in which the most heat is produced (wikipedia).

[323] The thermal theory of affinity postulated that the heat evolved in a chemical reaction was the true measure of its affinity.

[324] Walther Nernst (1864-1941) `https://en.wikipedia.org/wiki/Walther_Nernst`. See K. Mendelssohn, *The world of Walther Nernst: the rise and fall of German Science 1864-1941* (ebook form from Plunket Lake Press, 2015; the original 1973).

very accurate, and Nernst proposed that in the $T \to 0$ limit

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P - \left(\frac{\partial \Delta H}{\partial T}\right)_P \to 0 \tag{24.3}$$

to remove all the difficulties.[325]

His assertion can be explained as follows: (24.2) is rewritten as

$$\begin{aligned} \Delta G &= -T\int_{T_0}^{T} \frac{(\Delta H - \Delta H(T_0))}{T^2} dT - T\int_{T_0}^{T} \frac{\Delta H(T_0)}{T^2} dT + \frac{\Delta G(T_0)}{T_0} T & (24.4) \\ &= -T\int_{T_0}^{T} \frac{(\Delta H - \Delta H(T_0))}{T^2} dT + \Delta H(T_0) - \frac{\Delta H(T_0)}{T_0} T + \frac{\Delta G(T_0)}{T_0} T. & (24.5) \end{aligned}$$

That is,

$$\Delta G = \Delta H(T_0) - T\int_{T_0}^{T} \frac{(\Delta H - \Delta H(T_0))}{T^2} dT + \frac{(\Delta G(T_0) - \Delta H(T_0))}{T_0} T. \tag{24.6}$$

Also integration by parts gives

$$\int_{T_0}^{T} \frac{(\Delta H - \Delta H(T_0))}{T^2} dT = -\left.\frac{(\Delta H - \Delta H(T_0))}{T}\right|_{T_0}^{T} + \int_{T_0}^{T} \frac{1}{T}\left(\frac{\partial \Delta H}{\partial T}\right)_P dT \tag{24.7}$$

Therefore, (24.6) now reads

$$\Delta G = \Delta H - T\int_{T_0}^{T} \frac{1}{T}\left(\frac{\partial \Delta H}{\partial T}\right)_P dT + \frac{(\Delta G(T_0) - \Delta H(T_0))}{T_0} T. \tag{24.8}$$

Note that L'Hospital's theorem implies that

$$\lim_{T\to 0} \frac{\Delta G - \Delta H}{T} = 0 \tag{24.9}$$

is equivalent to Nernst's proposal (24.3). Thus, according to his proposal, we get

$$\Delta G = \Delta H - T\int_{0}^{T} \frac{1}{T}\left(\frac{\partial \Delta H}{\partial T}\right)_P dT. \tag{24.10}$$

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[325] Unfortunately in the $T_0 \to 0$ limit, the last term in (24.2) may not be finite, but ignoring this fact, Nernst 'demonstrated' this assertion. Here, a corrected demonstration will be given instead of the original dubious version.

24.3 Consequences of Nernst's assertion: The third law of thermodynamics

(24.1) and (24.9) imply

$$\lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right)_P = 0. \tag{24.11}$$

That is,

$$\lim_{T\to 0}\Delta S = 0. \tag{24.12}$$

This implies that the integral in the formal expression (24.10) must be finite and well defined. Thus, the reaction heat completely determines the free energy change (affinity) due to a reaction.

(24.12) means that for the totality of equilibrium states of the systems that can be transformed with reversible processes (including the changes of the materialistic 'stages' as discussed in **4.8**), their entropy densities at $T = 0$ are identical. In other words, all the reversible changes at $T = 0$ occur without any entropy change. This statement (24.12), or the formulas on which this statement is based, such as (24.3) or (24.9), are called *the third law of thermodynamics* or *Nernst's principle*.[326]

24.4 Reversible sectors of equilibrium states

Nernst's principle tells us that we can choose a common origin of entropy for any system mutually related by reversible processes. We may call such a set of systems a *reversible sector*.

The distinction between different sectors may become serious when we consider chemical reactions. For example, since we cannot synthesize any ^{13}C organic compounds from ^{12}C compounds, the systems consisting of these chemicals make two distinct reversible sectors. Thus, the the origin of entropy for each sector may be different.

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[326] ⟪**Nernst's joke on the three principles**⟫ Kurt Mendelssohn writes, "When lecturing on 'his' heat theorem, Nernst was careful to point to an interesting numerical phenomenon concerning the discovery of the three fundamental laws of thermodynamics. The first one had three authors, Mayer, Joule and Helmholtz; the second had two, Carnot and Clausius; whereas the third was the work of one man only, Nernst. This showed conclusively that thermodynamics was now complete since the authorship of a hypothetical fourth law would have to be zero." (*The world of Walther Nernst: the rise and fall of German Science 1864-1941* (ebook form from Plunket Lake Press, 2015; the original 1973) Chapter 4.

In organic chemistry, the compounds in different sectors may participate in chemical reactions. ^{12}C compounds and ^{13}C compounds can react to make 'mixed' chemicals. A natural question is: even if such 'intersector processes' can occur, can we still arbitrarily choose the entropy origins? Yes, we can, because there is no process in the usual thermodynamics that connect the ^{12}C world and the ^{13}C world reversibly. Therefore, there is no empirical means to check any entropy difference between these two worlds. Thus, we are free to choose the origin of different reversible sectors (if something is not observable, you can conveniently assume anything you wish about it[327]).

24.5 Nernst-Planck's theorem

24.3 tells us that the value of the entropy in the $T \to 0$ limit can be anything as long as it is bounded from below. We know empirically that there is no such tendency of divergence.

Planck recognized that this means that the entropy origin for each reversible sector can be set 0. Thus,

$$\lim_{T\to 0} S = 0 \tag{24.13}$$

is called the *Nernst-Planck theorem*.

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[327] In more detail: what we can obtain is the 'cost' to bring A and B from some starting points to AB. The costs to bring A and B to their starting points depend on their conventions. Thus, the total costs of making AB depends on all the costs A and B inherit, but as long as these inherited costs are consistently given in their own worlds, no inconsistency shows up.

25 Chemical reactions and chemical equilibria: Outline

This section provides an overview of the basic concepts of chemical thermodynamics that are typically covered in standard thermodynamics textbooks. It should be noted that any mathematically incorrect or flawed explanations and discussions in traditional thermodynamics have been rectified.

25.1 The expression of material constitution of a system: summary

Even in a closed system, the amount of chemicals can change (→**4.4**), depending on the system internal energy and work coordinates $(E, \boldsymbol{X})$; this set is called the *ordinary thermodynamic coordinates* (→**4.5**). This can cause various complications as discussed in **4.5**-**4.12**, but it was rather long ago (Section 4), so here let us review the problems.

The key point is that "the operations the experimenter can perform" and "the observations the experimenter can make" on the materials composition of the system must be distinguished and must be expressed in terms of different variables.

The mole numbers of chemicals that the experimenter can add to or remove from the system individually (→**4.8**) are called the materials coordinates (or chemical coordinates). For example, the totality $\boldsymbol{N}$ of the moles of the chemicals used to construct the system to study can be chosen to describe the materials coordinates of the system. The materials coordinates will dictate the materials constitution (chemical composition) as long as the system is closed, even if chemical reactions occur. Needless to say, the materials coordinates must be updated every time new chemicals are added (for the detail see **25.5**)

According to the principle II in **4.3**, when the materials coordinates of the system are $\boldsymbol{N}$, for each ordinary thermodynamic coordinate value set $(E, \boldsymbol{X})$ the system chemical composition variables $\tilde{\boldsymbol{N}}$, the amounts of chemicals currently present in the system, are determined—the reaction map $R : \tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\boldsymbol{N})$ determines the equilibrium chemical composition $\tilde{\boldsymbol{N}}$ based on $E, \boldsymbol{X}$ and $\boldsymbol{N}$.

For the detailed distinction between the materials coordinates and the chemical composition variables review **4.9**. The next unit illustrates chemical variables (materials coordinates or chemical composition variables) of a system with a simple reaction.

25.2 Materials coordinates, a simple illustration

As an example, let us use the chemical reaction (∗) in **4.5**.

$$\mathrm{A} + \mathrm{B} \longleftrightarrow \mathrm{C}.$$

For simplicity, the system has a unit volume that is kept constant, so that the molarities and the moles of the chemicals are numerically identical.[328] Let us assume the following equilibrium condition:

$$[\mathrm{C}]/[\mathrm{A}][\mathrm{B}] = K = 1, \tag{25.1}$$

where [X] denotes the molarity of chemical X.

(1) Suppose we prepare a system with 2 moles each of A and B. In this case the materials coordinates of the system may be chosen, for example, as $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (2, 2, 0)$. The equilibrium composition may be computed as follows: When the above reaction reaches an equilibrium, x moles each of A and B are consumed and x moles of C is formed, so (25.1) implies $x/(2 - x)^2 = 1$, which implies $x = 1$ in equilibrium. Hence, the actual chemical composition of the system may be written as $(\tilde{N}_\mathrm{A}, \tilde{N}_\mathrm{B}, \tilde{N}_\mathrm{C}) = (1, 1, 1)$. If you wish, you could update the materials coordinates of the system as $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (1, 1, 1)$, although this is not required; there are infinitely many possible choices of materials coordinates that give identical chemical composition (→**25.6**) for a given system.

(2) For the reaction system in (1) if, for example, we change E (or its temperature) while the system is still closed, let us assume that the equilibrium constant K in (25.1) (→**25.21**) is modified to be $K = 3$. Then, the equilibrium composition is given by $(\tilde{N}_\mathrm{A}, \tilde{N}_\mathrm{B}, \tilde{N}_\mathrm{C}) = (2/3, 2/3, 4/3)$. Needless to say, its materials coordinates can still be chosen as $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (2, 2, 0)$ (or, if we updated as suggested at the end of (1), $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (1, 1, 1)$) as before. Of course, we can further update the materials coordinates to be $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (2/3, 2/3, 4/3)$, if you wish.

(3) To prepare the system under consideration we only need to prepare the system according to one of the many equivalent materials coordinate expressions of the system. For example, we can prepare the same system with 2 moles of C only. In this case the materials coordinates of the system can be $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (0, 0, 2)$, but in the state with $K = 1$ (25.1) implies $(2 - x)/x^2 = 1$, where x is the moles of C decomposed. Thus, $x = 1$. That is, the system chemical composition is, just as in (1), $(\tilde{N}_\mathrm{A}, \tilde{N}_\mathrm{B}, \tilde{N}_\mathrm{C}) = (1, 1, 1)$ (which is not equal to $(2, 0, 0) + (0, 2, 0)$).

(4) These are cases in which reactions occur spontaneously in the system, but we could prepare the system by combining two half-volume systems. Suppose we prepare a system with volume 1/2 containing only 2 moles of A (its materials coordinates are $(2, 0, 0)$ and so are its chemical composition) and a system with volume 1/2 containing only 2 moles of B (its materials coordinates are $(0, 2, 0)$ and so are its chemical composition). Combine these two systems to make a volume 1 system with the materials coordinates given by

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[328] In many cases for liquid systems, there is a ‘solvent’ that does not participate in the reactions. We ignore the solvent in this example.

$(2,0,0)+(0,2,0)=(2,2,0)$. The resultant chemical compositions are not additive due to chemical reactions, and many different states may result according to K. For example, if $K=1$ (as shown in (1)) the chemical composition is $(1,1,1)$.

(5) Let us add 2 moles of C to the system prepared in (1). The materials coordinates of the system become $(2,2,0)+(0,0,2)=(2,2,2)$. If we wish to choose the materials coordinates of the system prepared in (1) to be $(1,1,1)$, the materials coordinates after adding 2 moles of C are $(1,1,3)$. If $K=1$ and if we choose the materials coordinates to be $(2,2,2)$, assuming that x moles of A is consumed before reaching chemical equilibrium, $(2+x)/(2-x)^2=1$, so $x=(5-\sqrt{17})/2$, that is, the resultant chemical composition is $((\sqrt{17}-1)/2,(\sqrt{17}-1)/2,(9-\sqrt{17})/2)$. If the materials coordinates are $(1,1,3)$, assuming that y moles of C is decomposed before reaching a chemical equilibrium, $(3-y)/(1+y)^2=1$, so $y=(-3+\sqrt{17})/2$ and the equilibrium chemical composition is $((\sqrt{17}-1)/2,(\sqrt{17}-1)/2,(9-\sqrt{17})/2)$ as before.

25.3 Independent chemical ingredients

There are two interpretations of the independence of chemicals for a given system (→**25.1**). One is the operational independence (can we add separately?) and the other the independence of changes of composition of the system. The latter independence is complicated and is hard to use (→**4.8**).

The materials coordinates are introduced to describe the operational independence, but the intrinsically accompanying chemicals mentioned in **4.8** make operational introduction of really pure substance into the system practically impossible. For example, to introduce a certain amount of water inevitably introduce certain amount of OH^-, H_3O^+, etc. Under constant T and P the amount of these accompanying compounds are uniquely fixed (due to the chemical equilibrium conditions). Therefore, even though in this case there are (at least) three chemicals, the equilibrium condition $2H_2O \longleftrightarrow H_3O^+ + OH^-$ and electroneutrality tell us only one of them is independently and operationally changed. Thus, usually, water is regarded as the independent chemical.[329]

As is clear, the number of independent chemical components is less than that of the independent materials coordinates due to chemical equilibrium relations. The following has already been stated clearly in **4.8** (ii), but is repeated just below because of its importance.

If we ignore accompanying chemicals, all the materials coordinates are independent. How about the chemical component variables? According to the elementary

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[329] However, the amounts of accompanying compounds change when the system state changes, since they are determined by chemical equlibria. In most cases, this effect is ignored.

chemistry principle II (→**4.3**), for a closed system, the chemical component variables are not thermodynamically independent variables at all.

25.4 Is there any way not to introduce two kinds of chemical variables?

We have introduced the materials coordinates and chemical composition coordinates, because the variation of the ordinary thermodynamic coordinates $(E, \boldsymbol{X})$ can vary chemical composition, even if we do not perform any experimental manipulation of chemicals. This causes mathematical dependence of chemical variables on $(E, \boldsymbol{X})$. Therefore, for example, the expression such as (in this unit, $\boldsymbol{N}$ is interpreted as in the conventional thermodynamics; not the materials coordinates, but generic chemical coordinates)

$$\left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},\boldsymbol{N}} \tag{25.2}$$

turns out to be extremely delicate (at best; meaningless if we follow the ordinary analysis).

To avoid such a difficulty, the standard chemical thermodynamics, if honest, assumes that $\boldsymbol{N}$ may be kept constant in any equilibrium state (that is, any chemical reaction may be frozen at will) without spoiling the thermodynamic equilibrium of the system under study. Indeed, this assumption decouples $\boldsymbol{N}$ and the ordinary thermodynamic coordinates to make $(E, \boldsymbol{X}, \boldsymbol{N})$ a set of genuine independent mathematical variables.

Since the second law is stated without chemical variables even in existing chemical thermodynamics textbooks, we must understand that the convexity and variational principles are all without chemical reactions (or 'favorably interpreted', under the assumption that the chemical composition is fixed).

When we wish to discuss chemical reactions thermodynamically, we wish to apply the thermodynamic variational principle (→**12.6**) to chemistry. However, with the above convention, it is impossible to show the concavity of entropy as a function of $(E, \boldsymbol{X}, \boldsymbol{N})$. Thus, no variational principle applicable to chemical reactions has been formulated.

To formulate chemical thermodynamics mathematically consistently, we need convex analysis in the space spanned by $(E, \boldsymbol{X}, \boldsymbol{N})$ without halting chemical reactions. Thus, we need two types of variables as summarized in **25.1**.

25.5 How to choose materials coordinates

Suppose we need $\boldsymbol{N}$ moles of chemicals to construct a system (as seen in **25.2** (3)) If the equilibrium state of this system is $(E, \boldsymbol{X}, \boldsymbol{N})$, its chemical components are given in terms of the reaction map (→**4.12**) as $\tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\boldsymbol{N})$.

There are many different ways to prepare the same system materially, so there are many ways to choose its materials coordinates. For example, even we can choose the current chemical composition $\tilde{\boldsymbol{N}} = \boldsymbol{n}$ as the value of $\boldsymbol{N}$, since trivially $(E, \boldsymbol{X}, \boldsymbol{N}) = (E, \boldsymbol{X}, \boldsymbol{n})$. There is a mathematically proper way to define $\boldsymbol{N}$ as an equivalence class consisting of the above mentioned 'many ways' as explained in **25.6**. However, this choice is inconvenient and rather unfamiliar to physicists, so more practical choices are discussed below.

The most important characteristics of the materials coordinates are the following two:

(I) When additivity is needed, as in convex analysis, we can always choose additive representation of the materials coordinates.

(II) When the result of chemical reactions is explicitly needed, we can choose the values of materials coordinates identical to the chemical composition variable. That is, choose $\boldsymbol{N} = \boldsymbol{N}^*$ such that $\boldsymbol{N}^* = R_{E,\boldsymbol{X}}(\boldsymbol{N}^*)$.

25.6 Mathematical expression of the materials coordinates and the representative elements[330]

When the ordinary thermodynamic coordinates of the system are given by the reaction map $(E, \boldsymbol{X})$, its materials coordinates $\boldsymbol{N}$ determine its chemical composition $\tilde{\boldsymbol{N}}$ as $\tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\boldsymbol{N})$ in terms of the reaction map (→**4.12**). There are infinitely many choices of materials coordinates that give the identical $\tilde{\boldsymbol{N}}$ as we have seen in **25.2**. Thermodynamically any choice of the materials coordinates is equivalent. That is, if we introduce the equivalence relation $\approx$ among materials coordinates as

$$\boldsymbol{N} \approx \boldsymbol{N}' \iff R_{E,\boldsymbol{X}}(\boldsymbol{N}) = R_{E,\boldsymbol{X}}(\boldsymbol{N}'), \tag{25.3}$$

mathematically the materials coordinates should be the equivalence class of the range of the materials coordinates ${\mathbb{R}^+}^D$, where D is the dimension of the materials coordinate space, i.e., the number of operationally independently modifiable chemicals, due to $\approx$. That is, the element of ${\mathbb{R}^+}^D/\approx$ corresponds to distinct materials coordinates.

If a chemical reaction 'b' is stoichiometric, we can algebraically express it as (→**25.9**, especially (25.9))

$$\sum \nu_i^b \mathrm{C}_i = 0. \tag{25.4}$$

Therefore, irrespective of $(E, \boldsymbol{X})$, if we use the reaction coordinate ξ^b for reaction b, we can write

$$\delta N_i = \nu_i^b \xi^b. \tag{25.5}$$

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[330] based on T. Tsujishita's input.

Therefore, if there are various reactions,

$$\delta N_i = \sum_r \nu_i^r \xi^r. \tag{25.6}$$

That is, the equivalence relation $\boldsymbol{N} \approx \boldsymbol{N}'$ is equivalent to the existence of ξ^r such that

$$N_i - N_i' = \sum_r \nu_i^b \xi^r. \tag{25.7}$$

If the reactions are not stoichiometric, then not only the so-called stoichiometric coefficients may depend on $(E, \boldsymbol{X})$, but existing chemicals themselves also depend on $(E, \boldsymbol{X})$. Consequently, we cannot rewrite the equivalence class determined by $R_{E,\boldsymbol{X}}$ in terms of simple chemical reaction formulas as above.

As noted in (2) of **25.5**, practically it is convenient to choose an appropriate member in an element of $\mathbb{R}^{+D}/\approx$.

25.7 Proposed practical choice of the materials coordinates $\boldsymbol{N}$

In conventional chemical thermodynamics textbooks, there is a requirement that chemical coordinates (typically corresponding to our chemical composition variables) can be freely frozen at any point. Subsequently, once the desired changes have been completed, chemical reactions are permitted to progress in order to attain a new state of chemical equilibrium. To adhere closely to this convention while avoiding any artificial and frequently unfeasible procedures, the following proposal could be considered the most suitable:

(I) When the system is in an equilibrium state, its material coordinates are set to agree with the current chemical composition variables of the system. All calculations involving derivatives in this state are carried out with respect to the chosen material coordinates.

(II) If certain chemicals are introduced (in an algebraic manner), the material coordinates are updated according to the following guidelines:

(II1) If the addition process is conducted quasistatically and reversibly, the material coordinates are updated in line with (I), signifying that the chemical composition variables of the final state are adopted as the material coordinates.

(II2) If the addition process lacks any specified conditions, then the updated material coordinates are the simple sum of the material coordinates from the initial equilibrium state and the added chemicals. The system will eventually attain a new equilibrium state, and the determination of the final material coordinates aligns with (I).

(III) In the case of a closed system, wherein we consider the quasistatic and reversible chemical reactions, we may designate the material coordinates as identical to the chemical composition variables for studying these reactions. Consequently, the chemical coordinates for a given system are the equilibrium material coordinates, denoted by $\boldsymbol{N} = \boldsymbol{N}^*$.

The base line is a follows
If no chemicals are introduced into the system, there is no requirement to revise the material coordinates, regardless of the system's developments. If the system is not closed, the material coordinates should be adjusted simply by incorporating the quantities of the added chemicals into the current material coordinates. In the context of chemical reactions taking place within a closed system, a practical approach is to utilize chemical composition variables; there is no obligation to consider them as the materials coordinates, if you prefer not to. Nevertheless, upon concluding all processes, it is advisable to update the material coordinates to agree with the final chemical composition variables.

25.8 The algebraic expression of chemical reactions

If chemicals A, B, C, $\cdots$ react to produce chemicals Z, Y, X, $\cdots$, the corresponding chemical changes or chemical reaction is represented by

$$a\ \mathrm{A} + b\ \mathrm{B} + c\ \mathrm{C} + \longrightarrow z\ \mathrm{Z} + y\ \mathrm{Y} + x\ \mathrm{X} + \cdots. \qquad (*)$$

Here, lower case letters are positive integers (usually) and are called stoichiometric coefficients.[331] Notice, however, that the above expression need not express the actually occurring reactions, but can be a summary of various reactions in parallel or a summary of a sequence of several reactions. Needless to say, the chemical reaction in a system need not be a single reaction.

In the above expression, the left-hand side is called the *original* or *reactant system* and the right-hand side is called the *product system*.

In thermodynamics it is convenient to write the above formula algebraically as

$$\sum_i \nu_i \mathrm{C}_i = 0. \qquad (25.8)$$

Here, ν_i is called the *generalized stoichiometric coefficient* for chemical C_i. The sign convention is: It is negative for the reactant system and positive for the product system.

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[331] Such expressions are enough for the usual chemistry and biochemistry, but for, e.g., geochemistry, many so-called nonstoichiometric compounds show up, so the coefficients need not be integers.

Many reactions can occur simultaneously in the system, so each reaction is distinguished with a superfix b, and (25.8) is more generally expressed as

$$\sum_i \nu_i^b \mathrm{C}_i = 0. \tag{25.9}$$

25.9 The extent of chemical reaction

Suppose in (25.8) the reaction proceeds to the right and the moles of chemical C_i (moles as the chemical composition in the system) changes by $\delta\tilde{N}_i$. This quantity and ν_i are proportional for all i and has the same sign. Therefore, we introduce the *extent of chemical reaction* ξ through the following differential form:

$$d\xi = \frac{d\tilde{N}_i}{\nu_i}. \tag{25.10}$$

If there are many chemical reactions in the system, the extent of the chemical reaction for each reaction will be distinguished with a subscript as ξ_b. Here, the reactions need not be 'independent.' The independence of reactions is just the linear independence of the chemical reactions expressed as (25.8) regarding C_i to be the basis vectors of a linear system.

25.10 What process does the chemical reaction formula express?

It is not entirely clear what (25.8) or $(*)$ of **25.8** actual represent as physical processes. If it only describes the chemical equilibrium relation, then the chemical potentials of the chemicals showing up on the both sides are determined by the equilibrium mixture. However, for example, according to Kirkwood-Oppenheim's *Chemical Thermodynamics* the reaction consists of the following three stages:

(a) Pure reactants are mixed under T, P.
(b) Chemical reactions are allowed to proceed.
(c) Pure products are separated from the product mixture.

According to Kirkwood a reaction implies the totality of (a) - (c). However, in many experiments, only stage (b) alone is studied. Kirkwood-Oppenheim states that for gas phase reactions (b) overwhelms, but in liquids mixing heats cannot be ignored, so corrections are required.

25.11 van't Hoff's equilibrium box

An apparatus to observe chemical equilibrium maintained by reaction $(*)$ of **25.8** (that is, the stage (b) of **25.10**) is proposed by van't Hoff (van't Hoff's reaction box). From the cylinders containing pure chemicals A, B, $\cdots$, Y, Z with selectively permeable membranes corresponding to them is constructed an apparatus illustrated in Fig. 25.1. Here, each piston is regulated to change each chemical i by $\nu_i d\xi$ according to (25.10).

The mixture in the big box is an equilibrium mixture, so the reactions proceed only quasistatically (→**25.16**). Actually, in chemical equilibria, no net reactions proceed, so to maintain equilibrium, we do not need any such device.

Figure 25.1: Van't Hoff's equilibrium box

With this device it is in principle possible to realize all the chemical potentials of pure substances in the cylinders participating in the reaction to be identical to the ones in the box by changing the pressures of the cylinders. Therefore, in principle, equilibrium thermodynamic experiments can be performed for any chemical reactions.

A summary is given in **25.12**.

Remark To perform equilibrium thermodynamic experiments some textbooks propose the use of 'negative catalysts' to slow down reactions. Usually, a catalyst is a small amount whose concentration may be ignorable, but kinetically it changes the reaction. This idea works to accelerate a reaction that hardly proceeds spontaneously. Here, however, we must kill the reactions that easily proceed spontaneously, so any effective negative catalyst must stoichiometrically block reacting chemicals. This is hardly realizable without changing the reaction mixture. Thus, negative catalysts should not be relied on as a means to regulate the reaction speed.

Remark We have discussed intrinsic accompanying compounds in **4.8**. Usually, minority accompanying compounds are ignored, even though the chemicals loaded in the cylinders are with intrinsic accompanying compounds. Unfortunately, there are cases of chemicals that are usually impossible to purify. Perhaps the most popular example may be $N_2O_4 \longleftrightarrow 2\ NO_2$. In this example, neither chemical can be isolated. Thus, we cannot even approximately use van't Hoff's reaction box. In such cases, the inseparable mixtures of chemical should be handled as a single substance.

25.12 Are reactions and mixing processes separated or not?

Imagine an ideal situation where the original system without any reaction ((a) of **25.10**) is first prepared, and then the reaction starts. This idealization cannot be realized since the reactions start immediately after chemicals are mixed before reaching mixing equilibrium.[332] Therefore, the original and reactant systems are both fictitious. Thus, such a question with the title of this unit occurs.[333]

If we can completely stop chemical reactions (as assumed by standard thermodynamics textbooks) by some means, then, van't Hoff's box allows us to measure the free energy changes for (a) and (c) in **25.10**, in principle. After preparing a reactant mixture, we can let the reaction proceed. However, the process cannot be a quasiequilibrium reversible process,[334] so, strictly speaking, we cannot apply thermodynamics.

The reaction we can discuss in thermodynamics is only chemical equilibrium. Using the van't Hoff's box containing the equilibrium mixture, we can measure the needed ΔG to prepare this mixture from the standard states of chemicals. In a quite parallel fashion, we can measure the needed ΔG to separate the mixture into products in their standard states. Therefore, we can measure the Gibbs energy change by the reversible quasistatic process converting the reactant system to the product system.

This is the ΔG for the totality of (a)-(c), and not (b) alone. However, we must look at the structure of chemical potentials. The activity or fugacity basically expresses (non-ideal) mixing entropy with chemical interactions. Therefore, when we write

$$\Delta G = \sum_i \nu_i \mu_i, \tag{25.11}$$

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[332] In the standard chemical thermodynamic textbooks, chemical reactions may be halted at any time without spoiling the system equilibrium. By this *deus ex machina* (a) and (b) of **25.10** are totally decoupled; we can freely prepare (a).

[333] However, electrochemically, in principle, decoupling of (a) and (b) is possible with the aid of van't Hoff box. See **25.7**.

[334] However, electrochemically, we may regulate chemical reactions to proceed quasistatic and reversibly.

usually, the effects of mixing and demixing of chemicals are included. If the chemical potentials μ_i are those for the equilibrium mixture in a van't Hoff reaction box, then $\Delta G = 0$.

Then, what is ΔG due to a chemical reaction?

25.13 Gibbs energy change due to chemical reactions

In the reaction (25.8) if the extent of reaction changes by $\delta\xi$,[335] the free energy change due to this reaction is written as

$$\delta G = \sum \mu_i \delta \tilde{N}_i = \delta\xi \left(\sum \nu_i \mu_i \right). \tag{25.12}$$

From this we see that the Gibbs energy change ΔG for a unit amount of this reaction (usually, 1 mole change for a chemical with $|\nu_i| = 1$) is given by

$$\Delta G = \sum \nu_i \mu_i. \tag{25.13}$$

Throughout this calculation we assume the system is closed and T, P constant.

Whether a reaction is thermodynamically permissible or not can be seen from the stability of the system. If T, P are constant, and if there is no other work than volume work (i.e., the usual case), according to the free energy minimization principle (→**19.7**) if $\Delta G > 0$ the reaction does not proceed (however, see **25.14**). If $\Delta G < 0$, thermodynamics does not object the advancement of the reaction to the right (that is, from the original or reactant to the product system). However, whether the reaction actually happens or not is a separate issue (see **12.4**)

Remark Notice that the usual thermodynamics textbooks do not explicitly state the second law applicable to chemical reactions, and since the chemical composition variables are used to describe the amounts of chemicals, it is hardly possible to justify the free energy minimization principle for chemical reactions in the existing textbooks.

25.14 Combinations making impossible possible

The essence of application of thermodynamics is to make a possible process through combining/coupling thermodynamically impossible processes and possible processes.

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[335] Since thermodynamics can discuss only equilibrium states, we can study only chemical reactions in equilibrium. Then, the reader may wonder how nonzero $\delta\xi$ is possible for a given equilibrium state. Precisely speaking, it is the result of thermodynamic variation (→**12.6**).

For chemical reactions a reaction with $\Delta G \ll 0$ and one with $\Delta G > 0$ may be coupled to advance the reaction with $\Delta G > 0$. Many biochemical reactions are such examples of this, and the wonders of biology are often realized by such couplings.[336]

As mentioned several times before, even if thermodynamics tells us that some reaction is 'very likely to occur (e.g., due to large negative ΔG), the relevant rate processes have nothing to do with thermodynamics. Consequently, to realize such a reaction requires a great deal of ingenuity, trial and error or evolution processes.

25.15 Chemical substances with zero concentration

For the reaction A+B $\longrightarrow$ C, if the concentration of C is zero or very close to zero, its chemical potential would be well approximated by the ideal solution formula (→**19.10**), so its chemical potential has an extremely large negative value. This suggests that the generalized work we can obtain (→**19.6**) from such a reaction could be very large. However, this never occurs. Why not?

This highlights the distinction between the ordinary work coordinates and the chemical composition variables. In contrast to most work coordinates, the change of chemical composition variables tend to deviate considerably from equilibrium as soon as the changing rate becomes non-zero. For the case of zero concentration chemicals, if we can wait sufficiently (i.e., if we can slow down the process sufficiently) considerably large amount of generalized work could be produced.

In contrast to the mechanical work, the thermodynamically expected results would not be obtained for the chemical work as soon as the rate becomes non-negligible.[337] There is indeed a qualitative difference between mechanical action and mass action.

25.16 Chemical reactions have equilibrium states: thermodynamic understanding

As shown in (25.13), when P and T are held constant, the chemical equilibrium

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[336] The origin of life itself is thought to be such an example. For example, just as we have demonstrated, a geochemically natural process coupled with reduction of carbon dioxide, which was impossible on the Hadean Earth, enables production of organic compounds [N. Kitadai et al., Metals likely promoted protometabolism in early ocean alkaline hydrothermal systems, Sci Adv 5 7848 (2020); Thioester synthesis through geoelectrochemical CO_2 fixation on Ni sulfide, Commun. Chem. **4**, 37 (2021)]. As seen in these papers, even electrochemical coupling, that should be far easier than the usual organic reaction coupling, requires special electrodes for the stage of chemical reactions. That is, even energetically possible coupling is hard to realize.

[337] As we will see later, this can be clearly observed in electrochemistry as 'overpotential.'

condition in a closed system is (as already noted in **19.5**)

$$\sum \nu_i \mu_i = 0. \tag{25.14}$$

The sum can be made as large as possible by reducing the concentrations of some chemicals in the reactant system. Instead, we can make the sum as small as possible by reducing the concentrations of some chemicals in the product system. The sum changes continuously, so we can always find a condition to satisfy the equilibrium condition. That is, for any reaction there is a chemical equilibrium. This means that thermodynamics and the elementary chemistry is consistent (→**4.3** II).

25.17 Nonuniqueness of materials coordinates and chemical equilibrium

Suppose $\boldsymbol{N}_1$ and $\boldsymbol{N}_2$ are equivalent materials coordinates for a system. This implies

$$R_{E,\boldsymbol{X}}(\boldsymbol{N}_1) = R_{E,\boldsymbol{X}}(\boldsymbol{N}_2) = \tilde{\boldsymbol{N}}. \tag{25.15}$$

The extensivity of G implies

$$\boldsymbol{\mu} \cdot \boldsymbol{N}_1 = \boldsymbol{\mu} \cdot \boldsymbol{N}_2 = \boldsymbol{\mu} \cdot \tilde{\boldsymbol{N}}. \tag{25.16}$$

In particular,

$$\boldsymbol{\mu} \cdot (\boldsymbol{N}_1 - \boldsymbol{N}_2) = 0. \tag{25.17}$$

This is of course consistent with **19.5** as long as chemical equilibrium is maintained, since $\boldsymbol{\mu}$ does not change:

$$\boldsymbol{\mu} \cdot d\boldsymbol{N} = 0. \tag{25.18}$$

25.18 Can we proceed chemical reactions quasistatically?

Thermodynamics can discuss, strictly speaking, only equilibrium. Then, when ΔG become large negative, isn't this conclusion meaningless? Since chemical reaction would proceed violently, nonequilibrium thermodynamics may be applicable. We have a glimpse of such situations in **25.15**.

Nevertheless, we should note the following two points:

(1) We can understand a given chemical reaction considerably, if we understand its chemical equilibrium and its stability. At least we can know the reaction is thermodynamically forbidden or not. Furthermore, needless to say, its chemical equilibrium

maybe studied quasistatically (→**25.16**).
(2) Electrochemistry allows us to construct electric cells from any reactions (in principle, at least). Even practically, many reactions allow us to construct electric cells to convert the mass action to mechanical work reversibly. Furthermore, its reaction rate may be controlled as needed. For example, an explosive reaction of hydrogen and oxygen could be observed near equilibrium reaction if we construct a fuel cell (→**??**). Even biochemical reactions such as the (half of the) TCA cycle could be used to construct an electric cell (→**??**). The importance of the principles of electrochemistry should not be underestimated for the foundations of chemical thermodynamics.
(3) Even if the whole process is not quasistatic, still there are cases we can apply equilibrium thermodynamics as has been noted in **??** (2). Thus, if a reaction does not proceed spontaneously, a catalyst can added to make the reaction possible, just as the pinhole between the gas canisters with different pressures. However, there exists a distinction between the reaction mixture and a gas leak. In the context of the reaction mixture, the reactant and product systems are typically not separated as gases at distinct pressures. If the reaction mixture is in a quasiequilibrium state (refer to **6.2**), there are no issues here. However, to be precise, since there is no equilibrium mixture close to the reaction mixture, we cannot employ equilibrium thermodynamics to describe the chemical potentials of the involved substances. In chemistry, however, if no spontaneous reactions happen, then the mixture is considered to be in an equilibrium state (recall **2.5**), so we are allowed to use equilibrium thermodynamics for reactions that do not proceed without catalysts.

How common are such reactions? We can assert that key physiological biochemical reactions cannot proceed without enzymes. Since cellular physiology must be meticulously regulated, spontaneity often disrupts intricate biological order.

25.19 The expression of chemical potentials

The chemical potential of chemical i with the partial pressure P_i in an ideal gas mixture is given by

$$\mu_i = \mu_i^{\ominus} + RT \log P_i. \tag{25.19}$$

Here, $\mu_i^{\ominus}$ is its chemical potential in the standard state (→**17.9**, **17.10**). For a general real gas, *fugacity* f is defined to maintain the shape of the formula (25.19) as much as possible to write

$$\mu_i = \mu_i^{\ominus} + RT \log f_i. \tag{25.20}$$

Needless to say, the fugacity must be determined empirically.

For an ideal liquid mixture the chemical potential of its component i with the molar fraction x_i is given by[338]

$$\mu_i = \mu_i^{\ominus} + RT \log x_i. \tag{25.21}$$

If the mixture is not ideal, the *activity* a_i is defined to replace the molar fraction to maintain the functional form of (25.21) as

$$\mu_i = \mu_i^{\ominus} + RT \log a_i. \tag{25.22}$$

25.20 How to obtain chemical composition from materials coordinates

The chemical equilibrium condition is

$$\sum_i \nu_i \mu_i(T, P, \boldsymbol{N}) = 0. \tag{25.23}$$

If the equilibrium chemical composition is $\tilde{\boldsymbol{N}}^e$, then we can choose the materials coordinates as $\boldsymbol{N} = \tilde{\boldsymbol{N}}^e$:

$$\sum_i \nu_i \mu_i(T, P, \tilde{\boldsymbol{N}}^e) = 0. \tag{25.24}$$

However, generally, we do not know $\tilde{\boldsymbol{N}}^e$ for a given $\boldsymbol{N}$ when the system is closed (or prepared). Therefore, we must be able to obtain $\tilde{\boldsymbol{N}}^e$ from $\boldsymbol{N}$ and (25.23). Notice that there must be the extent of reaction ξ such that

$$\tilde{\boldsymbol{N}}^e = \boldsymbol{N} + \boldsymbol{\nu}\xi, \tag{25.25}$$

where $\boldsymbol{\nu} = (\nu_1, \nu_2, \cdots)$. Since μ_i are expressed in terms of $\tilde{\boldsymbol{N}}$, we must find ξ such that

$$\sum_i \nu_i \mu_i \left(T, P, \boldsymbol{N} + \boldsymbol{\nu}\xi\right) = 0. \tag{25.26}$$

Here, $\boldsymbol{N}$ may be the initial composition before the chemical reaction occurs. Due to the convexity of G with respect to $\boldsymbol{N}$, (25.26) has a unique solution for ξ.[339] Thus, we can obtain $\tilde{\boldsymbol{N}}^e$ from (25.25).

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[338] There are different choices for the standard state (→**??**), here, the pure state (i.e., $x_i = 1$) is chosen as the standard state.

[339] Precisely speaking, the extremal set need not be a point, but must be a convex set. This means that the resultant equilibrium states can continuously change. Such an example must be extremely rare, if known at all.

25.21 Equilibrium condition for a chemical reaction: the law of mass action

The equilibrium condition[340] for the reaction (25.8) is given by

$$0 = \sum \nu_i \mu_i = \sum_i \nu_i \left[\mu_i^\ominus + RT \log a_i\right]. \tag{25.27}$$

This formula can be rewritten as

$$-\Delta G^\ominus \equiv -\sum_i \nu_i \mu_i^\ominus(T,P) = RT \log\left(\prod_i a_i^{\nu_i}\right). \tag{25.28}$$

The middle expression in the above does not depend on the system composition, so we may define the *chemical equilibrium constant* dependent only on T and P as

$$K(T,P) = e^{-\Delta G^\ominus/RT} = \frac{\cdots a_p^{\nu_p} \cdots}{\cdots a_r^{-\nu_r} \cdots}. \tag{25.29}$$

Here, the chemicals appearing the numerator of the right-hand side are all chemical in the original/reactant system and those on the denominator are chemicals of the product system. (25.29) is called the *law of mass action*. All the exponents are positive.

A large K implies that the reaction shifts to the product system (to the right). The following expression is intuitive and useful:

$$-\Delta G^\ominus = RT \log K. \tag{25.30}$$

As seen from this $-\Delta G$ is chemically very useful (see electromotive force in electrochemistry **??** or **??**), so this quantity is called chemical *affinity*.

It is claimed that “the equilibrium constants can be computed, in principle, statistical-mechanically,” but, except for the reactions among ideal gas species, the computation of needed chemical potentials is almost impossible, so especially for interesting reactions theoretical calculations are useless.

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[340] We assume that the system is closed. In some cases we may use chemostats, but then we must pay extra care not to realize nonequilibrium steady states. It is therefore wise to impose closedness conditions.

25.22 Changes in equilibrium condition: Le Chatelier's principle

If we differentiate the chemical equilibrium constant with T, we can get the reaction heat, i.e., the enthalpy change ΔH due to the reaction. Due to the Gibbs-Helmholtz relation (or its Gibbs energy version (19.7)) we have

$$\left(\frac{\partial \log K}{\partial T}\right)_{P,\boldsymbol{N}} = \frac{\Delta H^{\ominus}}{RT^2}. \tag{25.31}$$

$\Delta H^{\ominus}$ is the enthalpy change in the standard state. The formula is called *van't Hoff's formula*.

Similarly, we can obtain

$$\left(\frac{\partial \log K}{\partial P}\right)_{T,\boldsymbol{N}} = -\frac{\Delta V^{\ominus}}{RT}. \tag{25.32}$$

Here, $\Delta V^{\ominus}$ is the volume change due to the reaction in the standard state. Notice that Δ in chemical reactions always denote (sum for the product system) − (sum for the original/reactant system).

(25.31) implies that if the reaction is exothermic, i.e., if $\Delta H^{\ominus} < 0$, then the equilibrium can be shifted to the direction producing less heat by increasing the system temperature (that is, K is reduced, so the rightward advance of the reaction becomes harder). This is an example of Le Chatelier's principle (→**22.8**) that the response of the system occurs in the direction to reduce the effect of external perturbations. (25.32) is also such an example. Needless to say, they show that the world is stable.

25.23 Le Chatelier's principle in terms of extent of reaction

Let us study how the extent of reaction ξ changes if, for example, T is changed under chemical equilibrium condition. There are two key points:

(1) the original (unperturbed) equilibrium chemical composition may be described in terms of materials coordinates whose values agree with the corresponding equilibrium chemical composition $\tilde{\boldsymbol{N}}^e$.

(2) the chemical composition change due to chemical reaction in the closed system may be described by the addition of chemicals $\delta\boldsymbol{N} = \{\nu_i d\xi\}$ from outside.[341]

The chemical equilibrium condition is given by $\sum \nu_i\mu_i = 0$ (→**19.5**). Therefore, after changing T and P, we must have

$$\sum_i \nu_i\mu_i(T+\delta T, P+\delta P, \xi+\delta\xi) = 0. \tag{25.33}$$

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[341] Needless to say, there is no net import of materials coordinates.

Taylor expanding this, we obtain

$$\sum_i \nu_i \left(-s_i \delta T + v_i \delta P + \sum_j \nu_j \mu_{i,j} d\xi \right) = 0, \tag{25.34}$$

where partial derivatives are given by

$$-s_i = \left(\frac{\partial \mu_i}{\partial T} \right)_{P,\boldsymbol{N}}, \quad \mu_{i,j} = \left(\frac{\partial \mu_i}{\partial N_J} \right)_{T,P.N_j^c}. \tag{25.35}$$

Therefore, we have

$$\sum_i \nu_i(-s_i)\delta T + \sum_i \nu_i v_i \delta P + \sum_i \nu_i \nu_j \mu_{i,j} \delta\xi = 0, \tag{25.36}$$

From this, $\Delta S = \sum \nu_i s_i$ is the entropy change for the unit chemical reaction extent, so, for example, under constant P we get

$$\left(\frac{\partial \xi}{\partial T} \right)_P = \frac{\Delta S}{\sum \nu_i \nu_i \mu_{i,j}}. \tag{25.37}$$

Since $\mu_{i,j}$ is positive definite, and $\Delta S = Q/T$ for an imported heat Q, an exothermic reaction ($Q < 0$ or $\Delta S < 0$) moves 'backward' when the temperature is increased.

How to pretend to proceed conventionally even if many quantities are mathematically meaningless:
First, the usual (standard) derivation is given. Then, it is critically demolished and possible approaches will be discussed that are not problematic in principle. Finally, probably the only possible consistent framework will be given.

The chemical equilibrium condition is given by $\sum \nu_i \mu_i = 0$ (→**19.5**). Therefore, after changing T and P, we must have

$$\sum_i \nu_i \mu_i (T + \delta T, P + \delta P, \xi + \delta\xi) = 0. \tag{25.38}$$

Taylor expanding this, we obtain

$$\sum_i \nu_i \left(-s_i \delta T + v_i \delta P + \sum_j \nu_j \mu_{i,j} d\xi \right) = 0, \tag{25.39}$$

where

$$\mu_{i,j} = \left(\frac{\partial \mu_i}{\partial \tilde{N}_j} \right)_{T,P,\tilde{N}_j^c}. \tag{25.40}$$

Here, chemical coordinates are chemical composition variables $\tilde{\boldsymbol{N}}$, since they are the only variables appearing in the conventional chemical thermodynamics. From this, $\Delta S = \sum \nu_i s_i$ is the entropy change for the unit chemical reaction extent, so, for example, under constant P we get

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{\Delta S}{\sum \nu_i \nu_i \mu_{i,j}}. \tag{25.41}$$

Thus, we have 'derived' (25.37).

The problem of this argument is that $\tilde{\boldsymbol{N}}$ are not independent variables, so the partial derivatives such as

$$-s_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,\tilde{\boldsymbol{N}}} \tag{25.42}$$

are not defined, because μ is defined only for equilibrium states $(T, P, \tilde{\boldsymbol{N}})$, and if $\tilde{\boldsymbol{N}}$ are fixed, then T cannot generally be varied in equilibrium.

One might define a C^∞ extension of a function μ defined only on the equilibrium manifold to its ε-tubular neighborhood as μ^∞ that agrees with μ on the equilibrium manifold. In this case partial derivatives such as (25.42) is calculated as

$$-s_i = \left(\frac{\partial \mu_i^\infty}{\partial T}\right)_{P,\tilde{\boldsymbol{N}}} \tag{25.43}$$

and the derivative (25.37) can be computed as the ratio of partial derivatives of μ^∞ correctly. However, only the ratio is free from the arbitrary choice of μ^∞ outside the equilibrium manifold, so it seems impossible to derive the Le Chatelier's principle.

There may be an approach to use thermodynamic variations **12.6**. A thermodynamic variation is defined by a spatial partition $\mathcal{P}$ of the system. Each part of $\mathcal{P}$ must have the same δT and δP in the present case:

$$\delta\mu_i = \sum_{k\in\mathcal{P}} \left(-s_i^k \delta T + v_i^k \delta P + \sum_i \nu_i \nu_i \mu_{i,j}^k d\xi^k\right), \tag{25.44}$$

where the partition result $\{\delta\xi^k\}_{k\in\mathcal{P}}$must be compatible with $\delta\xi$. Unfortunately, ξ is not an additive variable, so the compatibility condition is complicated. Therefore, although in contrast to the standard argument there is nothing in the above formula that is mathematically illegal even in terms of the chemical composition variables, we cannot tell the sign of the partial derivative (25.37) from this.

25.24 Shift of chemical equilibrium due to added chemicals

For a closed system, the equilibrium shift is possible only by changing T, P or operational coordinates other than E and V. This can be understood through appropriate generalization of **25.23**.

Now, let us assume that the system is not closed, and materials coordinates are changed by $\delta\boldsymbol{N}$ under constant T and P. The equilibrium condition must be

$$\sum_i \nu_i\mu_i(T, P, \tilde{\boldsymbol{N}}^e + \delta\boldsymbol{N}) = 0. \tag{25.45}$$

Here, we assume that the system is in equilibrium before perturbation, so its materials coordinates may be chosen as $\boldsymbol{N} = \tilde{\boldsymbol{N}}^e$. The resultant equilibrium state can be obtained as discussed in **25.20**. The point is that all the chemical potentials are expressed in terms of the values of chemical composition $\tilde{\boldsymbol{N}}$. The key point is that the variables we use are materials coordinates $\boldsymbol{N}$, but their values are given by the current chemical composition:

$$\sum_i \nu_i\mu_i\left(T, P, \tilde{\boldsymbol{N}}^e + \delta\boldsymbol{N} + \boldsymbol{\nu}\delta\xi\right) = 0. \tag{25.46}$$

In terms of components, we can rewrite this, after expansion, as

$$\sum_{ij} \nu_i\mu_{i,j}(\delta N_j + \nu_j\delta\xi) = 0. \tag{25.47}$$

For example, if we change only N_1, we get

$$\sum_i \nu_i\mu_{i,1}\delta N_1 = -\sum_{ij} \nu_i\nu_j\mu_{i,j}\delta\xi. \tag{25.48}$$

That is,

$$\frac{d^*\xi}{d^*N_1} = -\frac{\sum_i \nu_i\mu_{i,1}}{\sum_{ij} \nu_i\nu_j\mu_{i,j}}. \tag{25.49}$$

Here d^*/d^*N_1 implies the derivative of the extent of reaction by adding only N_1 under constant T and P while allowing all the chemical compositions to vary.[342] Since the system is stable, the denominator is positive. Maxwell's relation implies $\mu_{i,1} = \mu_{1,i}$, so the above formula implies

$$\frac{d^*\xi}{d^*N_1} = -\frac{1}{\sum_{ij} \nu_i\nu_j\mu_{i,j}}\left(\frac{\partial\mu_1}{\partial\xi}\right)_{T,P}. \tag{25.50}$$

Therefore,

$$\frac{d^*\xi}{d^*N_1}\left(\frac{\partial\mu_1}{\partial\xi}\right)_{T,P} < 0 \tag{25.51}$$

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[342] Notice that all the materials coordinates other than N_1 are kept constant.

That is, if its chemical potential is reduced when the reaction proceed to the right (toward the production side), then adding the chemical promotes the reaction. Generally speaking, adding N_1 increases its chemical potential (just as exothermic reaction increases the system temperature), so the reaction opposes this tendency.

When such an inequality as (25.51) is applied (more generally, when we consider le-Chatelier-principle-related relations are used), do not forget the conditions under which the the relations are derived. Thus, for (25.51) do not forget that T and P are fixed.[343]

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[343] A good expository article may be found in Y. Yoshimura' s homepage `http://khem2022.starfree.jp/index.htm`: "There is a counterexample for Le Chatelier's principle?". This was introduced to the author by Prof. Y. Tanimura.

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